U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
PB80-107055

Evaluation of Methodology and Prototype to Measure Atmospheric Sulfuric Acid

Atlantic Research Corp, Alexandria, VA

Prepared for

Environmental Sciences Research Lab, Research Triangle Park, NC

Aug 79

United States
Environmental Protection
Agency

Environmental Sciences Research
Laboratory
Research Triangle Park NC 27711

EPA-600/2-79-168
August 1979

PB80-1[illegible]7055

Research and Development

Evaluation of Methodology and Prototype to Measure Atmospheric Sulfuric Acid

Final Report

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-79-168	2.	3. RECIPIENT'S ACCESSION NO. PB 80 107055
4. TITLE AND SUBTITLE EVALUATION OF METHODOLOGY AND PROTOTYPE TO MEASURE ATMOSPHERIC SULFURIC ACID Final Report		5. REPORT DATE August 1979 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) R. E. Snyder, M. E. Tonkin, and A. M. McKissick		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Atlantic Research Corporation 5390 Cherokee Avenue Alexandria, VA 22314		10. PROGRAM ELEMENT NO. 1AA601B CA-036 (FY-79) 11. CONTRACT/GRANT NO. 68-02-2467
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U. S. Environmental Protection Agency Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final 9/76-11/78 14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES

Interim Report: EPA-600/2-77-010, January 1977

16. ABSTRACT

A method has been developed to selectively assay ambient sulfuric acid aerosol. The method utilizes the vapor of a volatile amine (or amine derivative) to neutralize the acid as it is collected on a Teflon filter. The amine sulfate thus formed is thermally decomposed at 200°C to release sulfur dioxide, or other stoichiometrically related sulfur containing adducts, which are measured by a flame photometric detector. Immediate chemical fixation of the acid lessens the chance of side reactions with other substances on the filter, while the relatively low decomposition temperatures aids in eliminating other sulfur-containing particles. Sulfur dioxide is also collected as a reagent complex on the filter, but is selectively removed by heating at 100°C.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Air pollution *Sulfuric acid *Aerosol Sulfur dioxide *Collecting methods Chemical analysis *Flame photometry *Prototypes		13B 07B 07D 14B

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 172
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE PCA08-A01

EPA Form 2220-1 (9-73)

EPA-600/2-79-168
August 1979

EVALUATION OF METHODOLOGY AND PROTOTYPE TO MEASURE ATMOSPHERIC SULFURIC ACID
Final Report

by

R. E. Snyder
M. E. Tonkin
A. M. McKissick
Atlantic Research Corporation
Alexandria, Virginia 22314

Contract No. 68-02-2467

Project Officer

Kenneth T. Krost
Atmospheric Chemistry and Physics Division
Environmental Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

1a

DISCLAIMER

This report has been reviewed by the Environmental Sciences Research Laboratory, U. S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U. S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

The objective of this study was to propose a promising methodology for the selective analysis of ambient sulfuric acid aerosol and to determine the feasibility of the method. The methodology was to cover the range of 0.25 to 50 $\mu g/m^3$. A review of the literature indicated that current analytical deficiencies revolved around an inability to selectively analyze the collected acid aerosol in the presence of interfering sulfates, and the loss of sulfuric acid during sample acquisition due to the formation of artifacts on the collection surface. Since little could be done to isolate interfering species from the acid aerosol during sample collection, a promising approach appeared to be that of reacting the acid aerosol prior to sample collection to form a stable adduct that could be selectively analyzed in the presence of interfering sulfates.

Theoretical consideration of reaction kinetics and aerosol sampling methodologies suggested that use of a volatile reagent which underwent an acid-base reaction with sulfuric acid was a promising approach. Interest then focused on volatile amines and amine derivatives which would react rapidly in the gas phase with sulfuric acid aerosol to form amine sulfate and bisulfate salts. Further consideration suggested that the adduct could be conveniently analyzed if it decomposed to evolve SO_2 gas at a temperature below that of interfering sulfates (<200 °C).

A reaction chamber was designed and constructed which allowed the flowing aerosol sample stream to mix with various fixing reagents. Adducts thus formed were collected on Millipore Teflon Filters of 5 and 0.5 micrometer pore size located at the end of the reaction chamber. A Teflon thermal decomposition cell was constructed in which the fixed acid samples were heated at 200°C to liberate SO_2. A valve arrangement connected the cell to a flame photometric detector (FPD) or a West-Gaeke bubbler which measured the evolved SO_2. It was established with this apparatus that the gas phase fixation process was very rapid and essentially complete during reaction chamber residence time. In addition, using this technique, a mass balance was obtained between predicted aerosol generator concentration (123 $\mu g/m^3$) and measured aerosol concentration (111 $\mu g/m^3$).

Ammonium sulfate, often present in ambient atmosphere was considered to be the primary positive interference. It was demonstrated that this interference was eliminated for H_2SO_4 aerosols in the 0.005 to 0.3 micrometer size range. However, the decomposition temperatures for various adducts made from 1.0 to 3.0 micrometer aerosols tended to overlap in some cases with those of the ammonium sulfate salts. It was determined that the side reaction between ammonia and sulfuric acid was suppressed on collection surfaces as the result of forming sulfuric acid during the collection process.

This report is submitted in fulfillment of Contract No. 68-02-2467 by Atlantic Research Corporation under the sponsorship of the U. S. Environmental Protection Agency. The report covers the period from September 30, 1976, through November 29, 1978.

CONTENTS

Abstract iii
Figures vi
Tables viii

1. Introduction 1
2. Conclusions. 3
3. Recommendations. 4
4. Technical Discussion 5
   General Atmospheric Constituents 5
   The Sulfuric Acid Measurement Problem. 15
   Theoretical Development of Research Approach 18
   Separation of Interfering Species. 33
   Summary of Theoretical Development 38
5. Experimental 41
   Aerosol Generation 41
   Aerosol Collection and Adduct Formation. 45
6. Results and Discussion 53
   Preliminary Experiments. 53
   Decomposition Characteristics of Adducts (Unmodified Thomas Generator - 0.005 to 0.3 μm Droplets) 62
   Decomposition Characteristic of Adducts (Baird Generator, 1 to 3 μm Droplets) 74
   Characteristics of Adduct Decomposition Gases. 84
   Modified Thomas Generator. 91
   Analysis of Concurrent Samples Using the Heated Sampling Device with NH_3 Fixing Reagent. 96
   Mass Balance 98
   Volatilization of H_2SO_4 (Modified Thomas Generator). . 99
   Field Tests. 111
   Summary. 124

References. 130

Appendices

A. Reactions in flow systems. 135
B. Measurement techniques for sulfuric acid and sulfuric acid aducts 147

FIGURES

Number Page

1 Total ion current chromatogram 9

2 Three principle size ranges for ambient particle size distribution. 14

3 Filter holder. 19

4 Bubbling system. 20

5 Impactor 21

6 Filter system with spray jets. 25

7 H_2SO_4 filter collection (gas or vapor reagent) 25

8 Thomas aerosol generator 43

9 Baird aerosol generator. 44

10 Sample and fixation apparatus. 46

11 Modified aerosol collection system 47

12 Revised sample decomposition chamber 49

13 Composite DTA of potential interferences 54

14 IR spectrum of a) diethylhydroxylamine sulfate, b) diethylhydroxylamine, and 3) sulfuric acid. 56

15 IR spectrum of a) acetaldoxime sulfate, b) acetaldoxime, and c) sulfuric acid 57

16 $(PDA)_2SO_4$ and Py_2SO_4 DTA 58

17 Early FPD recordings from samples. 59

18 Effect of injecting progressively larger SO_2 volumes 60

19 Quantitative FPD response to injected SO_2. 61

20 Quantitative response of FPD to SO_2. 61

21 Completeness of fixation by AAO (fixed temperature procedure). . 65

22 Completeness of decomposition of AAO/H_2SO_4 adduct after 5 min (A) and 15 min (B) 66

23 Typical FPD trace from AAO-treated sample. 67

24 AAO-fixed filter portions after heating 5 min at 200°C 68

25 AAO-treated samples, different sampling volumes, 5 min at 200°C. 69

Number Page

26 Pairs of AAO-fixed samples collected simultaneously 70

27 Continuous heating procedure - FPD recordings from H_2SO_4 and adduct samples 73

28 Relationship of aerosol sample volume and evolved SO_2 from AAO adduct decomposition 83

29 Submicron particles fixed with ammonia ten minutes after sample collection 116

30 Submicron particles fixed with ammonia during sample collection . 116

31 Decomposition profile of NMF-SO_4 adduct 117

32 Decomposition profile of AAO-SO_4 adduct 117

33 Composite decomposition profile - AAO-SO_4, NMF-SO_4, $(NH_4)_2SO_4$ . . 118

TABLES

Number		Page
1	Organic Components of Industrial Waste Effluents.	6
2	Approximate Elemental Concentrations Found in Particulates Collected from Ambient Urban Air	10
3	Variation of Sulfuric Acid Content of Atmospheric Aerosols. . .	13
4	Comparison of Instruments	22
5	General Reactions of Sulfuric Acid.	27
6	Decomposition Temperatures of Ambient Sulfates.	34
7	Temperature of Initial FPD Response from Adducts (Unmodified Thomas Generator)	63
8	Peak Heights of Sample Pairs Collected Simultaneously	70
9	Temperature (°C) of First FPD Response from Sulfur Gas-Reagent Complexes	72
10	Initial H_2SO_4 Decomposition Temperature by H_2SO_4 Generation Method	75
11	Initial H_2SO_4 Adduct Decomposition Temperatures by H_2SO_4 Generation Method	76
12	Summary of $(NH_4)_2SO_4$ Decomposition Temperatures for Various Sample Sizes.	78
13	Initial Response of FPD for $(NH_4)_2SO_4$ by Deposition Method. . .	79
14	Recovery of SO_2 From AAO/H_2SO_4 Adduct (Dry Air)	81
15	Recovery of SO_2 From AAO/H_2SO_4 Adduct (Humidified Air).	82
16	Specificity of West-Gaeke Technique for SO_2	85
17	Turbidimetric Analysis of Raw H_2SO_4	86
18	Sulfuric Acid/AAO Adduct Analysis (LS Filter-Turbidimetric Analysis)	86
19	Decomposition Efficiency of AAO Adduct.	87
20	Decomposition of DEA Adduct (SO_2 Analysis).	88
21	Percent Loss of Various Adducts Due to Reaction With Ammonia. .	91
22	Analysis of Concurrent Samples Using Ammonia Fixing Reagent . .	93
23	Analysis of Concurrent Samples Using Diethylamine Fixing Reagent	93

Number		Page
24	Concurrent and Sequential NH_3 Derivative Samples.	96
25	Concurrent and Sequential NH_3 Derivative Samples with Number 1 Leg Heated (105°C)	97
26	Comparison of Predicted and Measured Aerosol Concentrations . .	99
27	Percent of Acid Passing Prefilters (123 $\mu g/m^3$).	100
28	Background Sulfur Levels as μg H_2SO_4.	101
29	Analysis of H_2SO_4 Aerosol at the 12.3 $\mu g/m^3$ Level (Ambient Conditions).	102
30	Heated Aerosol Collection at the 12.3 $\mu g/m^3$ Level (Sample Rate 9 l/min)	103
31	Heated Aerosol Collection at the 61 $\mu g/m^3$ Level (Sample Rate 9 l/min)	103
32	Analysis of Samples Taken at the Prefilter (Modified Thomas Generator - No Flame).	105
33	Analysis of Samples Taken at the Collection Filter (Modified Thomas Generator - No Flame).	106
34	H_2SO_4 Slip Through Prefilter at 145°C (Modified Thomas Generator - No Flame).	107
35	Quantitative Recovery of H_2SO_4 Passed Through the Prefilter (Modified Thomas Generator)	108
36	Passage of H_2SO_4 Droplets Through Prefilter at 190°C (Modified Thomas Generator - With Flame).	109
37	Passage of H_2SO_4 Droplets Through Prefilter Using H_3PO_4 Scrubbed Air (Modified Thomas Generator - With Flame)	109
38	Passage of H_2SO_4 Droplets Through Prefilter at 190°C Versus Time (Modified Thomas Generator - With Flame).	110
39	Animal Chamber Tests (Prefilter and Collection Filter).	114
40	Animal Chamber Studies - All Quantitative Samples Taken by ARC on 7/19/78	120
41	Animal Chamber Studies - All Quantitative Samples Taken by ARC on 7/20/78	120
42	Animal Chamber Studies - Individual Sample Comparison Between EPA and ARC Samples	121
43	Animal Chamber Studies - Daily Average Data Summary Comparison Between EPA and ARC Samples.	122
44	Animal Chamber Studies - Average Data (Questionable Sample Deleted)	122
45	Results of Environmental Field Tests - Rural Area	123
46	Results of Environmental Field Tests - Urban Area	123

SECTION 1

INTRODUCTION

The concern regarding environmental sulfuric acid aerosol has been gradually gaining momentum over the years. This is due in part to recent smog disasters in Meuse Valley (1), Donora (2), and London (3). The inability to correlate mortality rates during these disasters with measured levels of sulfur dioxide has raised serious questions as to the real nature of the problem. Leighton (4) has documented that sulfur dioxide, in the presence of oxygen, moisture and sunlight can form sulfuric acid. This fact, coupled with the knowledge that high levels of sulfur dioxide existed during these smog disasters, has made sulfuric acid aerosol a prime suspect for responsibility for the excessive mortality rate. Firket's (5) correlation between ambient air particulates and mortality rates during the Meuse Valley smog disaster also suggests that aerosols could be responsible for the large number of deaths. Sulfuric acid is known to be a potent irritant that can cause narrowed air passages (6,7) and, thus, be a significant health hazard to people with respiratory difficulties.

The source of most H_2SO_4 pollution is fuel, which often contains significant quantities of sulfur. When fuel containing a sulfur component is burned, sulfur dioxide is generated. The sulfur dioxide, in the presence of oxygen, moisture and sunlight, can be further oxidized to sulfuric acid. The process can be accelerated by metal particulates in the air which serve as catalysts.

The current energy crisis suggests that more coal will be used in the future as an energy alternative. Much of our coal resources has a high sulfur content which will cause ambient sulfate levels to rise. The advent of the automobile catalytic converter insures efficient oxidation of SO_2 to H_2SO_4 (or a sulfate salt) and will also add to the problem.

Thus, the ambient sulfate situation shows no sign of improvement, but only a steady upward trend can be anticipated.

The hazards that can result from H_2SO_4 aerosols in ambient air make it imperative that a reliable method for its measurement be established. Many problems in finding a method for measuring H_2SO_4 in air can be foreseen. The primary problem is the diversity of forms in which aerosols exists, i.e., sulfuric acid, ammonium sulfate and metal sulfates, some of which are water soluble (Na_2SO_4), and some of which are insoluble ($PbSO_4$). In order to accurately measure sulfuric acid concentration, both the sampling and analysis method must be capable of handling all forms of sulfate efficiently. Other problems which affect the reliability of a method are the collection of small particles, the loss of H_2SO_4 by reaction with other particulates, and interferences from various pollutants.

SECTION 2

CONCLUSIONS

Sulfuric acid can react on collection surfaces with other environmental particulates during sample collection to form other compounds and thus cause a negative interference. This effect can be lessened by the in situ addition of a gaseous reagent into the moving gas sample stream which will subsequantly react with the sulfuric acid to form a more stable adduct. Reaction kinetics indicate that adduct formation in a moving gas stream is best accomplished by volatile basic reagents capable of undergoing protonation. Volatile amines and amine derivatives appear to be ideal for the in situ gas phase fixation of sulfuric acid.

Positive interferences during the analysis of sulfuric acid adducts were limited to sulfur bearing species by using the sulfur specific flame photometric detector. Interferences were further eliminated by selecting fixing reagents which form sulfuric acid adducts that thermally decomposed below the thermal decomposition temperature of potentially interfering sulfates. It could not be determined if ammonium sulfate salts were totally eliminated using the thermal decomposition/flame photometric technique due to the absence of a suitable referee analysis method for the low levels (0.1 - 3 μg) of sulfuric acid found in the environment. An alternate approach for eliminating ammonium sulfate interference by volatilizing the sulfuric acid aerosol and selectively passing it through a prefilter was found to be inefficient at volatilization temperatures up to 200°C. The sulfur gases SO_2, COS, and H_2S were found not to interfere.

The gas phase fixation/thermal decomposition methodology exhibits good precision ($C_v = 0.20$) and good accuracy (±20%) for laboratory generated aerosols. The laboratory generation of accurate, reproducible sulfuric acid aerosols in the low $\mu g/m^3$ range is probably at least as difficult as sample collection and subsequent analysis. The combined lower sensitivity of the fixation/thermal decomposition approach utilizing the flame photometric detector is on the order of 0.05 μg H_2SO_4.

SECTION 3

RECOMMENDATIONS

As a result of the effort at Atlantic Research Corporation under Environmental Protection Agency Contract No. 68-02/2467, the following recommendations are made:

1) More field tests need to be performed in order to compare the gas phase/thermal decomposition concept with other potential sulfuric acid measurement methodologies. Field tests must be performed in order to evaluate the effect of ambient particle size dispersions on thermal decomposition temperatures of both sulfuric acid adducts and potential sulfate interferences.
2) Other derivatives should be evaluated for analysis by an alternate approach should the thermal decomposition approach be found unacceptable due to particle size effects. These derivatives should be evaluated using both laboratory-generated and field samples.

SECTION 4

TECHNICAL DISCUSSION

GENERAL ATMOSPHERIC CONSTITUENTS

The air we breath is a mixture of constituents occurring from natural life processes and the substances man generates as a result of his life style. The latter is the basis for the current epidemiological interest in air pollution. It appears that man is slowly poisoning himself with the by-products of his own inventiveness.

Industrial manufacturing processes sometimes have substances associated with them that are potentially dangerous as environmental contaminants. This problem is especially acute in immediate geographical industrial areas, since the concentrations may be quite high due to the close proximity of the emanating source. These substances can enter the environment in the form of gases, vapors, fumes, aerosols, or dusts, and hence, require a variety of pollution monitoring and control techniques. Generally, these substances originate from initial process materials or are by-products of the manufacturing process itself. As can be seen from Table 1 (8), a wide range of chemical species and manufacturing processes are associated with potential environmental hazards.

Fuel consumption is probably the largest source of environmental pollution. It has been estimated that the amount of sulfur introduced into the atmosphere by energy generation (coal, gas, gasoline) is equivalent to the combined emissions of all anaerobic processes and from volcanism (9). The largest single source of CO in the environment has been reported to be from the internal-combustion engine (10).

Recent studies have shown a direct correlation between inefficient fuel consumption and hydrocarbons found in the environment (11,12,13). Pellizzari, et al. (14) analyzed the atmosphere in several locations using porous polymers to concentrate trace pollutants. A chromatogram of an air sample taken in Glendora, California, using this concentration technique

TABLE 1. ORGANIC COMPONENTS OF INDUSTRIAL WASTE EFFLUENTS (8)

Plant	Composition
Mines, ore treatment plants	Humus, coal sludge, flotation agents, particulates, gases
Foundries	Cyanides, phenol, tar components, coal sludge
Iron and steel processing	Wetting agents and lubricants, cyanides, inhibitors, hydrocarbons, solvent residues
Coal production, coking plants	Humus, coal particles, cyanides, rodanines, phenols, hydrocarbons, pyridine bases
Wood charcoal production	Fatty acids, alcohols, particularly methanol, phenols, carbon monoxide
Petroleum industry	Oil emulsions, naphthenic acids, phenols, sulfonates, hydrocarbons, sulfur gases
Sulfite pulp	Methanol, cymol, furfurol, soluble carbohydrates, lignosulfonic acids, sulfur gases
Soda (sulfate) pulp	Mercaptans and sulfides, alcohols, terpenes, lignin, resinic acids, soluble carbohydrates
Rayon and cellulose	Xanthogenates, alkali hemicelluloses, toxic gases
Paper manufacture	Resinic acids, polysaccharides, mucins, cellulose fibers, flotation agents, sulfur gases
Textile industry	Scouring and wetting agents, leveling agents, sizers, desizing agents, fatty acids, finishes, Trilon (nitrilotriacetic acid), dyes
Laundries	Detergents: carboxymethylcellulose, enzymes, optical brighteners, colorants; soil: protein, blood, cocoa, coffee, carbohydrates, emulsified fats, soot

TABLE 1 (continued)

Plant	Composition
Leather and tanning industry	Protein degradation products, soaps, tanning agents, emulsified lime soap, hair
Natural glue and gelatin	Protein degradation products, emulsified fats and lime soaps
Sugar refineries	Sugar, plant acids, betaine, pectin and other soluble plant components.
Starch plants	Water-soluble plant components (protein compounds, pectins, soluble carbohydrates)
Dairies	Milk components (protein, lactose, lactic acid, fat emulsions), washing and rinsing agents.
Grease and soap factories	Glycerine, fatty acids, fat emulsions
Canning factories	All types of soluble plant components and volatile gases
Sauerkraut factories	Lactic, acetic and butyric acids, carbohydrates, other soluble plant components and gaseous constituents
Beer breweries	Water-soluble plant components, beer residues, rinsing agents
Fermentation industry	Fatty and amino acids, alcohols, unfermented carbohydrates
Slaughter houses	Blood, water-soluble and emulsified meat components, fecal matter

is shown in Figure 1, along with the identification of most of the atmospheric constituents. Clearly, the majority of the identified constituents can be attributed to fuel oils and gasoline. Nitrous oxide and sulfur dioxide, which are also major atmospheric pollutants, are primarily formed in combustion processes where nitrogen and sulfur are oxidized slowly by oxygen and more rapidly by ozone.

Particulate emissions are also characteristic of many aspects of a modern industrial society. Perhaps the most notorious source of these emissions is the internal-combustion automobile engine. Inorganic salts (especially lead), iron as oxides, base metals, soot, carbonaceous materials and tars constitute the primary components of these emissions (15).

In addition, industry, agriculture, utilities and the private sector make their own contributions to particulate pollution. While some of these emissions are from natural sources, such as wind erosion of soils, most are man-made. Trace metals, carbon-adsorbed gases, and various benzene-soluble organics have all been detected in urban atmospheres. Table 2 shows the results of elemental analysis of particulates found in the atmospheres of six cities (16).

Sulfuric Acid Aerosol and Sulfates

Sulfuric acid aerosols in the atmosphere are generally believed to be formed from the oxidation of SO_2 to SO_3 in the presence of ultraviolet light. It is the mechanism of the SO_2 oxidation that has been the subject of much scientific speculation for years. The postulated mechanisms fall broadly into two general classifications: Homogeneous and heterogeneous reaction processes. The literature reveals that homogeneous gas phase reactions (17-19) suffer from a lack of rate constant data, while the experimental evidence on heterogeneous processes (20,21,22,23) tend to disagree from one investigator to another. Thus, while many scientific theories have been postulated, none has totally fulfilled the scrutiny of scientific examination for the oxidation of environmental SO_2 to the corresponding acid aerosol. It would appear that both homogeneous and heterogeneous processes, along with other factors, simultaneously influence the rate at which SO_2 is oxidized by ultraviolet light. For example, it has

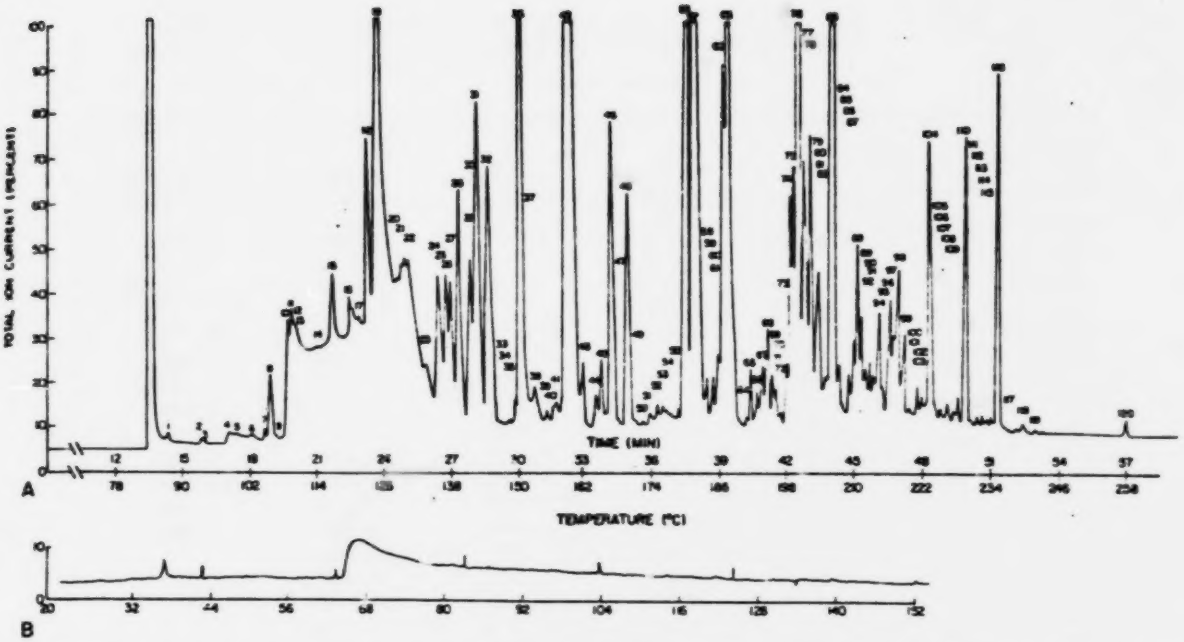


Figure 1. (A) Total ion current chromatogram of ambient air sample from Glendora, Calif. A 400 ft OV-101 SCOT programmed from 20 to 230 °C at 4 °C/min was used. (B) Total ion current chromatogram of Tenax GC cartridge blank. A 400 ft OV-101 SCOT was used. (14)

(1) Difluorochloromethane; (2) 1-butene; (3) isobutane; (4) unknown; (5) unknown; (6) isopentane, trichlorofluoromethane; (7) 1-pentene, C_5H_8; (8) *n*-pentane; (9) isoprene; (10) methylene chloride; (11) propanal; (12) acetone; (13) unknown; (14) unknown; (15) 2-methylpentane, 2-fluoro-2-methylpropane; (16) 3-methylpentane; (17) C_6H_{12}; (18) 3-methyl-2-pentene + *n*-hexane, 2-methylfuran; (19) chloroform; (20) C_6H_{14}; (21) C_6H_{12}; (22) methyl vinyl ketone (tent.), methyl ethyl ketone; (23) 1,1,1-trichloroethane, ethyl acetate; (24) benzene; (25) carbon tetrachloride; (26) C_6H_{12}; (27) 2,3-dimethylpentane; (28) 1,1,3,3-tetramethylcyclopentane; (29) cyclohexenol isomer; (30) unknown; (31) 1-*trans*-2-dimethylcyclopentane, C_7H_{16}, C_7H_{12}, trichloroethylene; (32) *n*-heptane; (33) C_7H_{12}; (34) C_8H_{14}; (35) 2,2,3,3-tetramethylbutane; (36) 4,4-dimethyl-2-pentene; (37) 2,5-dimethylhexane; (38) 3-heptene; (39) C_8H_{16}; (40) 1-octene; (41) 2,3-dimethylhexane; (42) toluene; (43) 2,4-dimethylhexane; (44) 2,2-dimethyl-3-ethylpentane; (45) trimethylcyclopentane isomer; (46) *n*-octane; (47) hexamethylcyclotrisiloxane; (48) tetrachloroethylene; (49) unknown; (50) 2,3,4-trimethylhexane; (51) C_8H_{16}; (52) C_9H_{20}; (53) *n*-butyl acetate; (54) C_9H_{18}; (55) chlorobenzene; (56) ethylbenzene; (57) *p*-xylene; (58) *m*-xylene; (59) 2,2,5,5-tetramethylhexane; (60) C_9H_{18}; (61) unknown; (62) C_9H_{20}; (63) *o*-xylene; (64, 65) $C_{10}H_{22}$ (isomers), C_9H_{18}; (66) $C_{10}H_{22}$; (67) isopropylbenzene, C_9H_{16}; (68) 2,6-dimethyloctane; (69) $C_{10}H_{20}$; (70) *n*-propylcyclohexane; (71) 4-ethyl-3-octene; (72) unknown; (73) 2-methyl-3-ethylheptane; (74) 4-methylnonane; (75) 5-methyldecane; (76) *n*-propylbenzene; (77) 2,6-dimethyloctane; (78) octamethylcyclotetrasiloxane; (79) $C_{11}H_{24}$; (80) *m*-ethyltoluene; (81) $C_{10}H_{20}$; (82) unknown, *n*-decane; (83) 1,3,5-trimethylbenzene; (84) unknown; (85) unknown; (86) isobutylbenzene; (87) *sec*-butylbenzene; (88) *m*-dichlorobenzene; (89) $C_{11}H_{24}$; (90) C_4-alkylbenzene; (91) 1,2,4-trimethylbenzene; (92) unknown; (93) unknown; (94) 4-ethyl-1-octyn-3-ol; (95) *o*-diethylbenzene; (96) *p*-propyltoluene; (97) *m*-diethylbenzene; (98, 99) $C_{11}H_{24}$ (isomers); (100) *sec*-butylbenzene; (101) 1,4-dimethyl-2-ethylbenzene; (102) $C_{11}H_{22}$; (103) 1,3-dimethyl-3-ethylbenzene; (104) *n*-undecane; (105) C_5-alkylbenzene; (106) $C_{11}H_{22}$, $C_{11}H_{20}$; (107) $C_{12}H_{26}$, $C_{11}H_{20}$; (108) *n*-dodecane; (109) 2,5-dimethyldecane; (110) unknown; (111) $C_{11}H_{20}$, $C_{12}H_{24}$; (112) $C_{11}H_{20}$; (113) $C_{12}H_{24}$, $C_{12}H_{26}$; (114) $C_{11}H_{24}$; (115) $C_{12}H_{26}$; (116) unknown; (117) $C_{11}H_{24}$; (118) $C_{12}H_{26}$; (119) naphthalene.

TABLE 2. APPROXIMATE ELEMENTAL CONCENTRATIONS FOUND IN PARTICULATES COLLECTED FROM AMBIENT URBAN AIR (16)

(Nanograms/M^3)

Element	Cincinnati	Denver	St.Louis	Washington	Chicago	Philadelphia
H	3,000.	5,000.	7,000.	3,000.	10,000.	4,000.
Li	5.	20.	10.	3.	2.	2.
Be	0.2	0.04	0.4	0.1	<0.1	0.05
B	10.	20.	30.	10.	5.	5.
C	30,000.	40,000.	60,000.	30,000.	100,000.	30,000.
N	3,000.	2,000.	6,000.	2,000.	10,000.	5,000.
F	40.	400.	200.	100.	30.	20.
Na	4,000.	10,000.	10,000.	1,000.	5,000.	1,000.
Mg	1,000.	1,000.	2,000.	1,000.	5,000.	5,000.
Al	2,000.	7,000.	3,000.	2,000.	2,000.	3,000.
Si	5,000.	40,000.	6,000.	5,000.	6,000.	10,000.
P	100.	300.	200.	30.	60.	50.
S	4,000.	3,000.	8,000.	4,000.	3,000.	3,000.
Cl	1,000.	5,000.	1,000.	300.	10,000.	4.
K	1,000.	10,000.	2,000.	1,000.	2,000.	1,000.
Ca	6,000.	6,000.	20,000.	3,000.	10,000.	8,000.
Sc	<1.	2.	1.	1.	3.	10.
Ti	200.	400.	300.	200.	300.	400.
V	10.	20.	20.	100.	100.	200.
Cr	20.	20.	20.	10.	20.	40.
Mn	100.	100.	50.	50.	100.	200.
Fe	5,000.	5,000.	5,000.	2,000.	4,000.	4,000.
Co	5.	5.	3.	5.	10.	20.
Ni	20.	30.	20.	50.	40.	100.
Cu	300.	500.	3,000.	400.	400.	200.
Zn	1,000.	200.	3,000.	400.	500.	500.
Ga	5.	4.	10.	5.	6.	6.
Ge	5.	3.	5.	4.	7.	<0.4
As	20.	5.	50.	20.	60.	10.
Se	4.	2.	10.	5.	2.	2.
Br	50.	200.	300.	200.	100.	20.
Rb	10.	100.	20.	5.	20.	20.
Sr	10.	100.	50.	10.	40.	40.
Y	3.	4.	2.	1.	1.	2.
Zr	4.	20.	10.	4.	4.	10.
Nb	0.4	2.	1.	0.3	0.5	0.3
Mo	2.	5.	3.	2.	3.	2.
Ru	<0.04	<0.06	<0.04	<0.01	<1.	<0.03
Rh	<0.04	<0.2	<0.1	<0.03	<0.06	<0.01
Pd	≤0.2	<1.	<0.4	<0.1	<0.3	<0.3
Ag	<1.	1.	20.	0.6	2.	0.6
Cd	2.	1.	5.	0.3	3.	1.

TABLE 2. APPROXIMATE ELEMENTAL CONCENTRATIONS FOUND IN PARTICULATES COLLECTED FROM AMBIENT URBAN AIR (Continued)

Element	Cincinnati	Denver	St. Louis	Washington	Chicago	Philadelphia
In	<2.	<3.	<2.	<0.5	<1.	<1.
Sn	100.	10.	50.	20.	20.	40.
Sb	8.	5.	8.	3.	8.	60.
Te	≤0.2	<0.2	5.	0.3	≤0.2	≤0.1
I	0.5	2.	2.	4.	≤0.7	0.01
Cs	0.4	1.	1.	3.	0.7	0.4
Ba	50.	300.	100.	100.	50.	40.
La	2.	20.	2.	4.	5.	20.
Ce	3.	20.	3.	3.	7.	20.
Pr	1.	4.	1.	1.	2.	4.
Nd	3.	10.	3.	3.	5.	7.
Sm	0.4	1.	0.6	0.5	2.	1.
Eu	<0.2	0.5	<0.4	0.1	0.3	0.2
Gd	<0.6	1.	<1.	0.3	2.	0.6
Tb	<0.1	0.1	<0.2	0.05	≤0.1	0.2
Dy	<0.3	1.	<0.6	0.2	0.3	0.6
Ho	<0.1	0.1	<0.2	0.03	0.1	0.1
Er	<0.3	0.5	<0.6	<0.3	≤0.2	0.3
Tm	<0.06	<0.2	<0.1	<0.03	≤0.1	0.06
Yb	<0.2	<1.	<0.4	<0.3	≤0.5	0.3
Lu	<0.1	0.3	<0.2	<0.02	<0.1	≤0.04
Hf	<0.04	<0.6	<0.2	<0.05	<0.3	0.2
Ta	<0.1	<0.3	<0.3	≤0.05	≤0.1	≤0.2
W	0.2	2.	0.5	0.1	1.	1.
Re	<0.02	<0.05	<0.06	<0.01	<0.05	<0.02
Os	<0.02	<0.1	<0.06	<0.02	<0.04	<0.03
Ir	<0.02	<0.05	<0.03	<0.01	<0.02	<0.06
Pt	<0.03	<0.1	<0.1	<0.02	<0.04	<0.03
Au	<0.1	<0.1	<0.03	<0.02	<0.1	<0.06
Hg	<0.04	<0.1	<0.1	<0.05	<0.04	<0.03
Tl	<0.03	0.1	<0.1	≤0.02	≤0.01	0.04
Pb	1,000.	3,000.	3,000.	2,000.	4,000.	2,000.
Bi	0.5	1.	2.	0.3	2.	0.6
Th	0.1	0.6	1.	0.05	0.4	0.2
U	0.2	0.3	2.	0.05	0.2	0.2

been shown that furnace operating conditions alone can enhance sulfur emissions being immediately oxidized to sulfur trioxide (24).

Takahashi, et al. (25) proposed a simplified three-step mechanism for formation of the acid aerosol by photooxidation of SO_2.

(1) Photooxidation of SO_2 followed by rapid combination with a water molecule

$$SO_2 \xrightarrow[h\nu]{O_2} SO_3 \xrightarrow{H_2O} H_2SO_4 \text{ (vapor)}$$

(2) Nucleation to a critical size by combination with several water and sulfuric acid vapor molecules

$$H_2SO_4\text{(vapor)} + H_2O\text{(vapor)} \xrightarrow[\text{nucleation}]{} (H_2SO_4)_n(H_2O)_m \text{ (embryo)}$$

(3) Growth of the embryo to a large aerosol particle through combination with additional water, sulfuric acid and other molecules

$$(H_2SO_4)_n(H_2O)_m\text{(embryo)} \xrightarrow{H_2SO_4,\ H_2O,\text{particulates}} \text{aerosol particle}$$

The photooxidation rate, the growth of the aerosol particle and thus the sulfuric acid concentration in each particle is affected by the relative humidity. During the growth period, sulfuric acid molecules condense on the embryo resulting in an increase in the sulfuric acid concentration. Simultaneously, water molecules are also condensing. The resulting particle will grow until an equilibrium is reached between the water vapor pressure and the ambient relative humidity. The net result is that the concentration of sulfuric acid in each aerosol particle is a function of its radius and the ambient relative humidity. Table 3 shows the sulfuric acid content of an individual aerosol droplet as a function of particle radius and relative humidity. These data are the results of theoretical calculations (26); however, evidence indicates that the concentrations are representative of actual aerosols.

Inspection of Table 3 shows that the weight percent of sulfuric acid in an individual aerosol particle decreases as the particle size and the relative humidity increase. For aerosols ranging from r = 0.1 to 1.0 μm, the average concentration ranges between 45 and 60 weight percent for 50 percent relative humidity and between 33 and 54 weight percent for 75 percent relative humidity. These concentration ranges will be encountered under normal conditions. However, in areas of high humidity or inversion conditions, the concentration per particle can drop to 18 percent or below.

TABLE 3. VARIATION OF SULFURIC ACID CONTENT OF ATMOSPHERIC AEROSOLS (26)

Particle radius µm	Relative humidity	Mole fraction of H_2SO_4	Weight % of H_2SO_4
1.0	100	0.04	18.5
	75	0.086	33.9
	50	0.132	45.3
	25	0.196	57.0
	10	0.258	65.4
0.5	100	0.06	25.8
	75	0.098	37.2
	50	0.140	47.1
	25	0.200	57.6
	10	0.267	66.5
0.2	100	0.104	38.7
	75	0.132	45.3
	50	0.175	53.6
	25	0.225	61.3
	10	0.289	68.9
0.1	100	0.154	49.8
	75	0.179	54.3
	50	0.215	59.9
	25	0.267	66.5
	10	0.327	72.6

It is under these high humidity-inversion conditions that high sulfuric acid concentrations in air and resulting fog disasters occur, even though the concentration per particle is low.

The foregoing discussion suggests that collection methods should be capable of handling particles from 1.0 µm to 0.1 µm. It now appears, however, that sulfuric acid aerosol generated in automobile catalytic converters may be in the 0.01 µm size range. Whitby (27) has suggested (Figure 2) that the ambient particle distribution consists of three principle size ranges. The ranges given by Whitby consist of particles with a mass mean

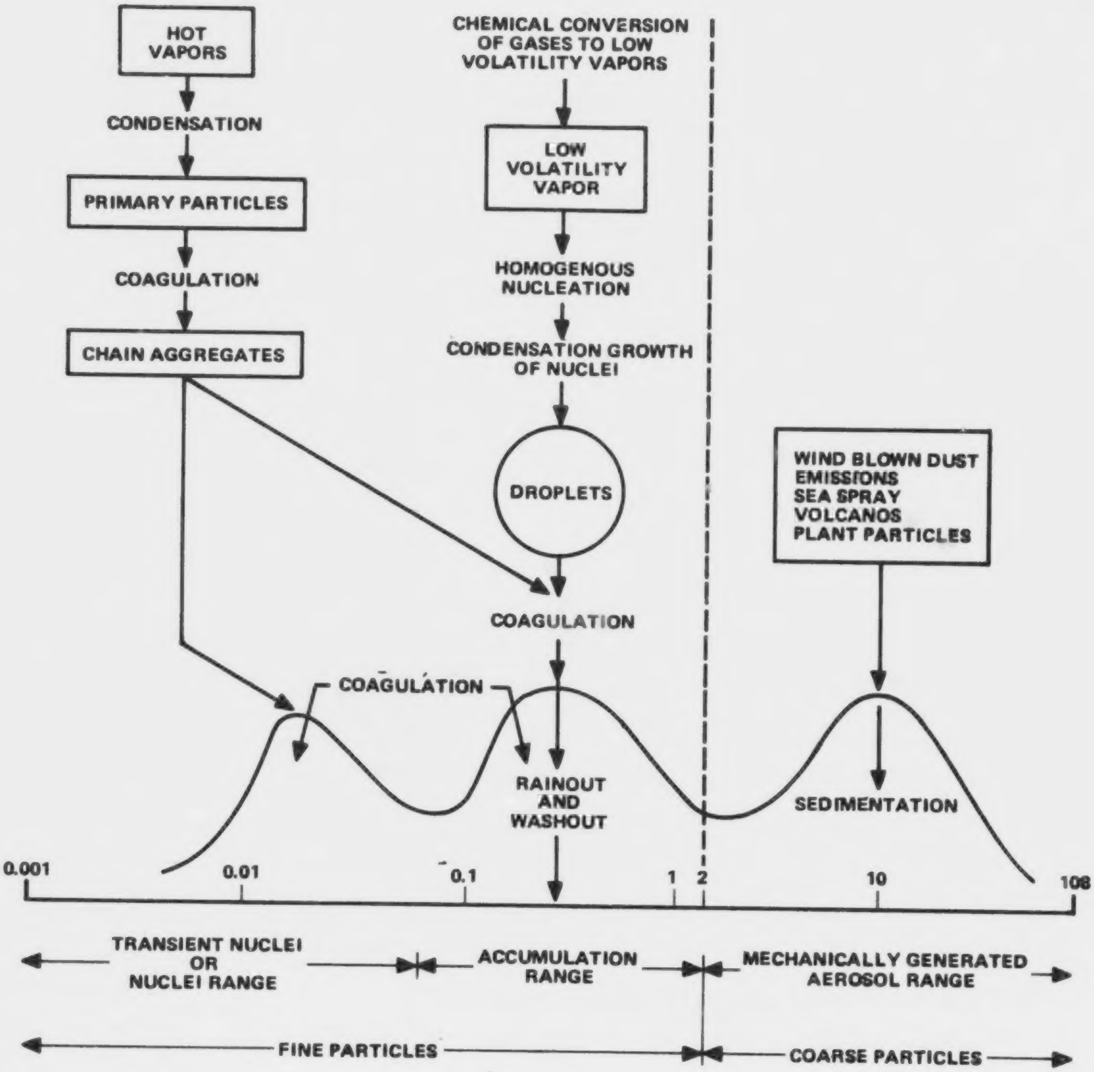

HOT VAPORS
CONDENSATION
PRIMARY PARTICLES
COAGULATION
CHAIN AGGREGATES
CHEMICAL CONVERSION OF GASES TO LOW VOLATILITY VAPORS
LOW VOLATILITY VAPOR
HOMOGENOUS NUCLEATION
CONDENSATION GROWTH OF NUCLEI
DROPLETS
COAGULATION
WIND BLOWN DUST
EMISSIONS
SEA SPRAY
VOLCANOS
PLANT PARTICLES
COAGULATION
RAINOUT AND WASHOUT
SEDIMENTATION
0.001
0.01
0.1
1
2
10
108
TRANSIENT NUCLEI OR NUCLEI RANGE
ACCUMULATION RANGE
MECHANICALLY GENERATED AEROSOL RANGE
FINE PARTICLES
COARSE PARTICLES

Figure 2. Three principle size ranges for ambient particle size distribution (27).

diameter of 10 μm, 0.4 μm and 0.02 μm. The 0.02 μm size range has serious health implications, since it is likely to penetrate further into the respiratory system causing severe chronic problems. Additionally, the smaller aerosol radius suggests an aerosol of higher sulfuric acid content. While these smaller aerosol particles are not likely to remain in the environment for extended periods, they should be considered as a serious threat to persons who are in close proximity to high traffic areas. Thus, development of any sampling/analytical method for sulfuric acid must necessarily consider particles in the 0.01 to 1.0 μm size range. As the burning of coals and high sulfur content fuel increases due to the energy shortage, a corresponding increase in the sulfate content of the ambient air can be anticipated.

THE SULFURIC ACID MEASUREMENT PROBLEM

It is likely that any atmospheric sample would contain many species and require special consideration to circumvent potential interferences during the analytical determination of a specific constituent within the sample matrix. This is especially true in the case of sulfuric acid aerosols, since sulfuric acid is well known for its propensity toward reaction with both inorganic and organic species. The reaction between sulfuric acid aerosol and other species can occur in the atmosphere, or it can occur on the sample collection surface as the result of enhanced physical contact between the acid aerosol and other enviromental constituents. By far the most difficult problem in the development of a method for measuring sulfuric acid aerosol has been the many potential interferences. These interference substances can be divided into two practical categories: those which artificially enhance the measured acid value (positive interference), and those which diminish it (negative interference).

Positive Interferences

Positive interferences usually result from the failure of an analytical method to distinguish between the desired compound and one which is chemically similar. This is particularly a problem with sulfuric acid measurement, because so many similar forms may be present in the atmospheric sample. Since the different forms are known to have different toxicological properties, it is necessary to be able to distinguish between them (28).

Ammonium sulfate and bisulfate have the greatest chemical similarity to sulfuric acid, and have constituted a severe interference with most previous methods of analysis. These compounds are formed by an equilibrium reaction between ambient ammonia and sulfuric acid, the extent of which seems to be related to climatic conditions (29). In aqueous solution, both sulfate and acidic protons (from hydrolysis of NH_4^+) are present, making it difficult to distinguish them from dilute sulfuric acid. Ammonium sulfate and bisulfate particulates in the atmosphere are generally associated with some moisture, futher enhancing the interference by hydrolysis which has already occurred. Some success has been achieved in separating H_2SO_4 from the ammonium sulfates by volatilization, since they are stable to about 235°C (30).

Many other sulfate salts may be present, some soluble (Na_2SO_4) and some insoluble ($CaSO_4$, $PbSO_4$). These are generally less of a problem than the ammonium sulfates, but may still interfere with a simple sulfate measurement. All but a few require temperatures over 500°C to cause decomposition, and none decompose under 250°C.

Ambient sulfur gases, including sulfur dioxide, hydrogen sulfide, carbonyl sulfide, and methyl mercaptan, can generally be separated automatically during collection, if a filtration or impaction system is used. There has been, however, some concern about the catalytic oxidation of SO_2 to sulfuric acid on certain filter media, particularly glass fiber filters (31). Other atmospheric particulates collected during sampling may also catalyze this reaction (31,32,33).

Also of concern are other strong mineral acids (HCl, HNO_3, and H_3PO_4) which may be present in an atmospheric sample (34,35). These may interfere directly if the analytical method measures only acidity, or they may interfere by reacting with sulfate salts on the collection surface to produce sulfuric acid.

Finally, a wide variety of substances may interfere with widely used wet chemical methods of sulfate analysis. Most of these methods are based upon precipitation of SO_4^{-2}, usually $BaSO_4$; thus, other anions which precipitate Ba^{+2} may interfere (PO_4^{-3}, S^{-2}). Some metal cations may cause a negative interference by precipitating sulfate (Pb^{+2}, Ca^{+2}), and other species may interfere by complexing indicator reagents. Clearly, a simple sulfate measurement is inappropriate unless the sulfuric acid is first separated from these other species.

Negative Interferences

Interferences that cause a negative error in analytical measurement generally result from loss of sample. Since sulfuric acid is a highly reactive substance, such a loss may readily occur if the acid contacts other particulates on the collection surface. Reactions with inorganic particulates can produce sulfate salts, which must necessarily be prevented if negative interferences from these compounds are to be avoided. Ambient ammonia may also cause a negative error, since the collection process tends to mix acid and ammonia to a greater extent than would normally occur. The product ammonium sulfates must be excluded from the sulfuric acid measurement.

These interfering side-reactions have been the greatest single obstacle in the development of a reliable measurement method for sulfuric acid aerosol. Volatilization techniques for separating the acid from its salts failed to prevent this sample loss; in fact, the loss may be increased by the volatilization procedure which brings hot acid vapor into contact with potentially reactive substances. Only by completely preventing these reactions can the interferences be avoided. By using a very sensitive analytical method which requires only a small volume of air to be sampled, the problem can be minimized, but not eliminated. Chemical stabilization of the acid as it is collected seems to be the only solution.

Approach to the Problem

From the foregoing discussion, it is evident that any solution to the selective measurement problem has several special requirements. In order to eliminate positive interferences, the method must be highly selective. Simple acid or sulfate measurement is not adequate unless sulfuric acid is first separated from other acids and sulfates in the atmospheric sample. To prevent negative interferences, the analytical method must be highly sensitive (so that only a small sample need be collected), and it must employ a process for chemically stabilizing the acid as it is collected. The choice of stabilizing (fixing) reagent is inherently limited by the sulfuric acid concentration in each aerosol particle as previously discussed. Of course, the sulfuric acid adduct thus formed must be selectively analyzable in the presence of many potentially interfering species.

It is also evident that each aspect of this problem is intimately related to every other aspect. Ideally, a combination of fixation, sampling, and analysis techniques, working together, would eliminate all interferences. No one of these three aspects can be regarded as separate from the other two, since a decision in any one area may limit possibilites for the other. The following discussion on theoretical development of research approach is divided into three main areas: aerosol sampling techniques, H_2SO_4 aerosol fixing reactions, and adduct sample analysis. Reference is made continually to all three areas.

THEORETICAL DEVELOPMENT OF RESEARCH APPROACH

Sulfuric Acid Aerosol Sample Collection

In any analytical scheme, it is obvious that interferences must be eliminated, or at least controlled, if meaningful quantitative results are to be obtained. In the case of sulfuric acid measurements, this is particularly difficult, since other sulfates and acids are present in the atmosphere, which tend to interfere with analytical tests. Ideally, the sampling method selected would capture only sulfuric acid molecules, and allow all others to escape. This would greatly simplify subsequent analytical procedures. Unfortunately, no selective collection system exists which will capture sulfuric acid aerosol and exclude other particulates. The following discussion describes current aerosol sample collection techniques and how they might be applied to the fixation of sulfuric acid aerosols.

Aerosol Collection Methods --

Filtration -- Collection of aerosol particles by filtration on a substrate is probably the most popular, as well as the most convenient and inexpensive method in use. Submicron particles, such as those found in aerosols, can be efficiently collected by this method.

The method as generally employed consists of a porous filter disc supported by a holder, as shown in Figure 3. The filter disc itself can be made of a number of different materials, such as common filter paper, glass fibers, wire screen, or membranes. Each type of filter material has inherent advantages and disadvantages, some of which are immediately obvious, and some not so obvious as shown by the following example.

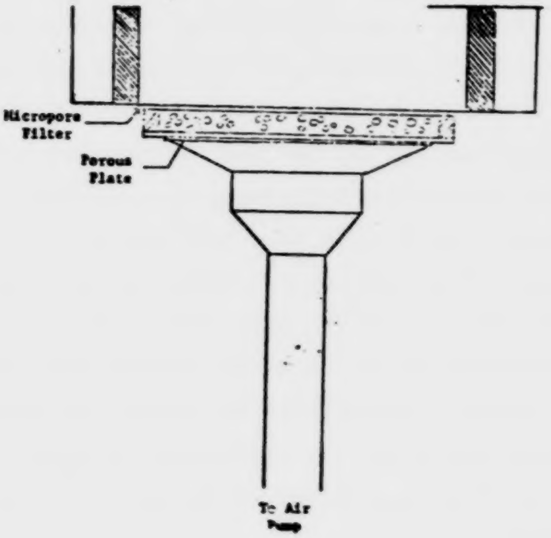


Figure 3. Filter holder.

Glass filters combine two desirable aspects of air sampling: high retention efficiency for submicron particles, and high flow rates. They have been frequently used for collection of aerosol sulfates. However, problems were discovered when glass filters were used for sulfate collection. Lee and Wagmen (36) showed that atmospheric SO_2 could be catalytically oxidized to SO_3 on the glass surface, thus giving high values for sulfate concentration. It has also been shown that sulfuric acid is irreversibly fixed in some glass fibers (24), and that many brands contain high amounts of sulfates (37). Any one of these factors can lead to erroneous results. Barton and McAdie (38) demonstrated that difficulties with glass filters can be overcome by pretreatment of the filters with sulfuric acid. However, Maddalone, *et al*. (38), found that treated glass filters were still troublesome and suggested the use of Teflon or graphite filter media for the collection of sulfuric acid aerosols.

Thomas, *et al*. (40), investigated Millipore, Whatman 41, Teflon, and graphite filters and found that Teflon filters were the least desirable with a collection efficiency of approximately 58 percent. In more recent work, however, West, *et al*.(41), have made use of Fluoropore Teflon filters and the glass fiber filters (42) found unacceptable by other researchers.

Liu, *et al* (43), used an electrical aerosol detector to determine the *in situ* collection efficiency of various filter media for specific monodisperse aerosols. Liu found that the Mitex LS filter media had a collection efficiency of approximately 100 percent on aerosols down to the 0.1 micron size range and a collection efficiency of approximately 90 percent at the 0.03 micron level. It is felt that Liu's work is more valid, because his data do not reflect the use of involved analytical chemistry methodology to measure the aerosol actually collected on the filter's surface. Instead, Liu measured the particle density distribution change as the aerosol stream passed through various collection media. Thus, it appears that the best media for the collection of H_2SO_4 aerosol by the filtration method is the 5 μm pore Mitex LS filter or the 0.5 μm pore Fluoropore Teflon filter.

Washing or Scrubbing -- Another class of H_2SO_4 aerosol sampling technique currently being used is the simple bubbling system shown in Figure 4.

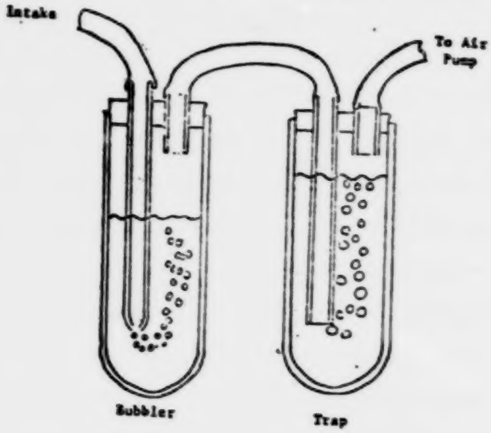


Figure 4. Bubbling system.

The method uses a liquid to facilitate the removal of aerosols from the air stream. A Greenburg-Smith impinger containing isopropyl alcohol is sometimes used for sampling sulfuric acid aerosols (24). The isopropyl alcohol serves to scrub the sulfuric acid and sulfur trioxide from the aerosol, while allowing the sulfur dioxide to pass through to another absorbing solution, usually hydrogen peroxide. The major disadvantage of this type of collection is the mist accompanying the effluent gas which can carry some of the initial aerosol with it. Difficulty also is often found in using this type of sampling when the component to be sampled exists in a variety of forms, as occurs in the case of sulfates. The problem is that most sulfate salts dissolve by the same mechanism as sulfuric acid, creating interferences.

Impaction -- The principle of operation of the impactor is based upon the differential momentum of gas and particulate matter in an aerosol stream. The direction of an aerosol stream is radically changed at a solid surface, and the particles are driven toward the surface and cling to it, as shown diagramatically in Figure 5. There are many instruments available which use variations of this principle for collecting aerosols down to the submicron range. Cascade impactors are capable of differentiating the aerosols by particle size. This is done by using a series of impaction points with jets of decreasing size. Inertial impactors use a rotating drum as the collection surface, which allows the time classification of particles. Other modifications of the collecting surface, such as metal foil for acid particles and glass plates immersed in liquid, have been used. The impaction method has been used by Scaringelli and Rehme (24) for particulate sizing and collecting of sulfuric acid.

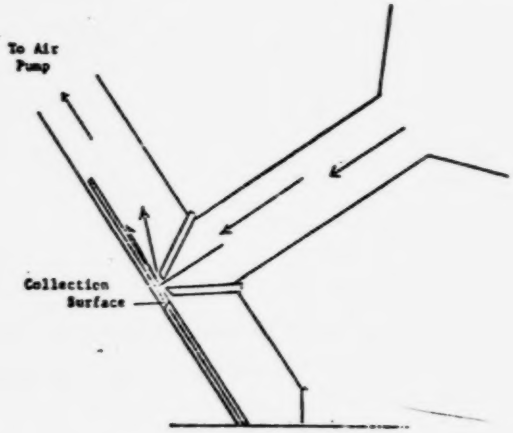


Figure 5. Impactor.

Precipitation -- Precipitation methods used in air pollution sampling include thermal and electrostatic precipitators. In thermal precipitation, the aerosol is passed between a hot wire which repels the particles and a cold plate where they are precipitated. Although this method is efficient, it has a low flow rate and sample capacity. The electrostatic precipitator, on the other hand, combines high flow rates, small pressure drop and high efficiency. Here, the gas stream is passed between a high electrical potential which drives the particles toward a collecting electrode where they are precipitated. Kerrigan, Snajberk and Andersen (44) used the electrostatic precipitator, the Greenburg-Smith impinger and the sintered glass filter method to collect a sulfuric acid aerosol for comparison purposes. The results of these tests are given in Table 4. It should be noted, however, that the H_2SO_4 concentration investigated was approximately one thousand times greater than the range of current environmental importance which is in the low $\mu g/m^3$ range.

TABLE 4. COMPARISON OF INSTRUMENTS (43)

	H_2SO_4 Mist Concentration, mg/m^3, as determined by:		
Test No.	**Precipitator**	**Impinger**	**Sintered Glass Filter**
1	18.4 16.9	18.0 17.2	17.9 17.2
2	28.0 26.8	29.0 28.9	28.6 32.2
3	24.8 27.4	26.2 25.0	24.3 22.9
4	72.3 69.1	69.8 69.5	67.9 72.2
5	30.7 31.6	31.1	33.5 31.3

Formation of H_2SO_4 Adduct During Sampling --

Each of the aerosol collection techniques discussed above is fairly efficient. The question here is how these techniques could be utilized in conjunction with a reagent to form a sulfuric acid adduct. In order to examine the relative merits of each collection method under these conditions, it must be assumed that a reagent which reacts specifically with sulfuric acid has been defined. It then becomes a matter of insuring contact between the sulfuric acid aerosol and the adduct-forming reagent during sample collection.

One problem that is inherent in all of the above-mentioned sampling techniques is that they tend to collect a variety of airborne particulates. There appears to be no feasible way to mechanically separate the sulfuric acid aerosol from other airborne particulates. If the collection medium is simply pre-coated with the adduct-forming reagent, airborne particulates could form a mat over it, inhibiting the subsequent adduct reaction. There is a statistical probability that any given H_2SO_4 droplet could strike one of these alien particles and react to form another compound. Even if this side reaction does not occur, there exists the problem of volatilization of the sulfuric acid aerosol. It becomes apparent that any sampling method must necessarily segregate H_2SO_4 from other particulates to prevent reaction from occurring. The sampling method must allow for immediate contact of the H_2SO_4 with the adduct-forming reagent.

The collection surface of the sampler could be made large enough that the probability of an H_2SO_4 droplet finding another particle and reacting with it is small. This does not, however, appear to be a likely solution, since sample collection would become a problem of interpreting a probability factor which is controlled by the greatest variable of all: the environment. The heavier the loading of other particulates in the sampling environment, the greater is the probability of this inter-reaction occurring.

A large excess of adduct-forming reagent is obviously desirable to insure sample contact, but it is equally important that the reagent be in a matrix that prevents other airborne particulates from masking the sulfuric acid aerosol. Several theoretical considerations to the problem of applying the adduct-forming reagent to the H_2SO_4 aerosol during sampling are discussed below.

Impinger-Bubbler Method -- The impinger-bubbler method probably presents the most obvious choice as far as maintaining good reagent surface contact area. With this method, the reagent solution would serve as the collecting medium and would also serve to segregate other particles from the H_2SO_4 aerosol. This would allow for optimum reagent surface/sulfuric acid contact with very little probability of side reactions occurring due to H_2SO_4 surface contact with other particulates.

The ideal collecting solvent is one in which dilute acid (mostly water) is immediately soluble, but sulfate salts are not sufficiently soluble to interfere. This method might utilize an anhydrous solvent which might help eliminate the subsequent hydrolysis of other sulfates to sulfuric acid. In any case, the relatively large amounts of water in acid aerosols would be difficult to remove effectively, even with an anhydrous solvent. Thus, it is probable that a certain amount of hydrolysis is unavoidable with the selective solvent approach. Once the sulfate is in solution, whether it is derived from sulfuric acid or originates from some other particulate is indistinguishable. Thus, the selective solvent approach does not appear to be a viable means of eliminating analytical sulfate interferences, even though it appears promising as a means of controlling side reactions.

Filtration, Impaction and Precipitation -- Filtration, impaction and precipitation sample collection methods tend to create problems with airborne particulates matting the collection surface. It, therefore, does not appear desirable to simply apply an adduct-forming reagent to the collection surface prior to the actual sampling. Several novel approaches to the application of the adduct reagent were hypothesized and are considered in the following paragraphs.

It appears that the simultaneous spraying of the adduct-forming reagent while the sample is being collected is a feasible approach. To accomplish this, a pressurized aerosol bottle would be required containing the adduct-forming reagent which could be sprayed onto the surface of the filter medium through a metering jet. This would automatically coat all airborne particulates as they are collected and greatly reduce the probability of H_2SO_4 aerosol reaction with other substances. Since the fixing reagent would be sprayed as a liquid, the potential for dissolution of other sulfate salts would, of course, exist. While this approach is more feasible than the bubbler method for collection, a selective solvent may still be necessary. An elementary design for such a collection system is shown in Figure 6.

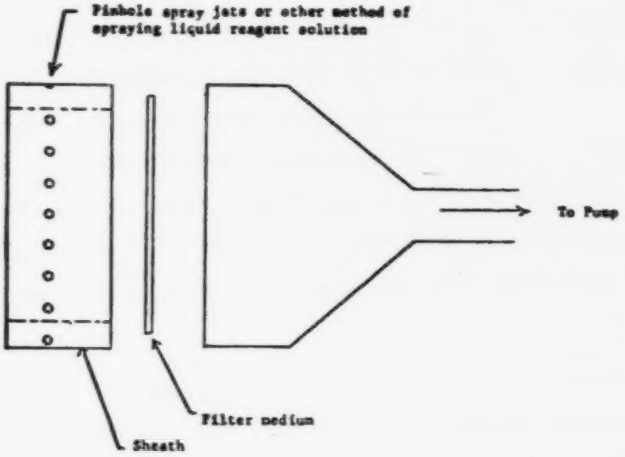

Pinhole spray jets or other method of spraying liquid reagent solution
To Pump
Filter medium
Sheath

Figure 6. Filter system with spray jets.

A better approach for a filter sampling system would be one in which the H_2SO_4 reacts with the adduct-forming reagent while the reagent is in the gas phase. This method, of course, would require a gas (vapor) with a fast reaction time. After being reacted in the sampling stream, the H_2SO_4 adduct could be collected on the filter medium while the residual vapor would pass through. A design for such a collection system is shown in Figure 7. It appears that the gas phase titration technique would be applicable to other collection techniques, such as impactors.

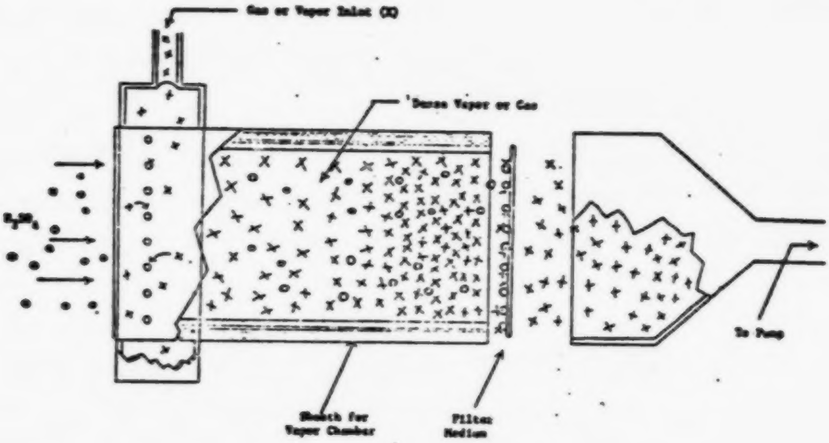

Gas or Vapor Inlet (X)
Dense Vapor or Gas
H_2SO_4
To Pump
Sheath for Vapor Chamber
Filter Medium

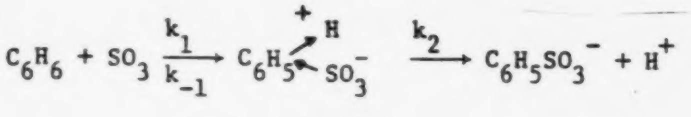
Figure 7. H_2SO_4 filter collection (gas or vapor reagent).

Sample Collection Conclusions -- Filtration or impaction sample collection techniques, coupled with gas phase adduct forming reagents, appear to offer the greatest potential for achieving the necessary aerosol contact. Gas phase fixation avoids the problems of solid phase fixation by providing better acid/reagent contact, preventing matting of the collection surface by continuously applying fresh reagent, and automatically removing excess reagent. The physical characteristics for the fixation of sulfuric acid aerosols in a gas flow system are reviewed in Appendix A. Selective solvent systems did not appear to be promising due to the solubility of other sulfate species collected at the same time as the acid aerosol.

Reaction Kinetics --

The following discussion considers the kinetics of reaction between sulfuric acid and various reagent classes to form sulfuric acid adducts. It is important that the adduct forming reaction takes place instantaneously in order to prevent the formation of artifacts during sample collection. The requirement that the fixing reagent react rapidly with sulfuric acid before side reactions occur can ultimately be defined only by observing the effect of possible interferences under actual sampling conditions. The final choice of fixing reagent will depend upon its ability to react rapidly and stoichiometrically with various concentrations of H_2SO_4 to form an adduct that can be selectively analyzed. Typical reactions of H_2SO_4 are given in Table 5 and consist of electrophilic aromatic substitution, electrophilic addition to alkenes, ester formation, oxidation-reduction reactions and acid-base reactions to form salts. Each of the above reaction classes are discussed in the following sections.

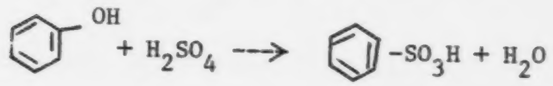
Electrophilic Aromatic Substitution -- One of the reaction types which sulfuric acid undergoes is electrophilic substitution on an aromatic ring (sulfonation). The mechanism of this substitution is postulated to be:



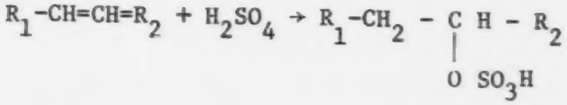
$$C_6H_6 + SO_3 \xrightarrow[k_{-1}]{k_1} C_6H_5\overset{+}{\begin{matrix} H \\ SO_3^- \end{matrix}} \xrightarrow{k_2} C_6H_5SO_3^- + H^+$$

TABLE 5. GENERAL REACTIONS OF SULFURIC ACID

I. Electrophilic Aromatic Substitution



II. Electrophilic Addition to Alkene



$$R_1\text{-}CH{=}CH{=}R_2 + H_2SO_4 \rightarrow R_1\text{-}CH_2 - \underset{\displaystyle O\,SO_3H}{\underset{|}{C}}\,H - R_2$$

III. Ester Formation

1. Primary Alcohols

$ROH + H_2SO_4 \rightarrow R\text{-}OSO_3H$

IV. Oxidation-Reduction

1. Inorganic

A. Metal

$xM + y\,H_2SO_4 \rightarrow M_x(SO_4)_y + H_2$

V. Acid-Base Reaction to Form Salts

A. Amines

$$\begin{array}{lcccl} R\text{-}NH_2 & & & & (RNH_3)^{+}{}_2SO_4^{=} \\ R_2\text{-}NH & + & \underline{H_2SO_4} & \rightarrow & (R_2NH_2^{+})_2SO_4^{=} \\ R_3\text{-}N & & & & (R_3NH^{+})_2SO_4^{=} \end{array}$$

milder conditions. However, steric hindrance may become a factor and the highly reactive carbonium ion may react with other anions.

The electrophilic addition of sulfuric acid to alkenes has some promise as a sulfuric acid fixing reagent. The probability of success is low due to the necessity to determine and control the reaction conditions in order to obtain reproducible results.

Sulfate Ester Formation -- Alcohols react with sulfuric acid or its anhydride to yield acid sulfate ester:

$$R\text{-}CH_2\text{-}CH_2\text{-}OH + H_2SO_4 \xrightarrow[k_H]{k} R\text{-}CH_2\text{-}CH_2\text{-}OSO_2OH + H_2O$$

Secondary alcohols react faster than primary. Once the acid sulfate is formed, it can undergo several reactions, depending upon the conditions. If the water content is high, hydrolysis occurs and the original alcohol is reformed. At higher temperatures and in the presence of HSO_4^-, the acid sulfate is dehydrated to the corresponding alkene:

$$R\text{-}CH_2\text{-}CH_2\text{-}OSO_2OH + HSO_4^- \xrightarrow[heat]{} R\text{-}CH{=}CH_2 + H_2SO_4 + HSO_4^-$$

or the dialkyl sulfate ester can be formed:

$$2R\text{-}CH_2\text{-}CH_2\text{-}OSO_2OH \longrightarrow (R\text{-}CH_2\text{-}CH_2)_2SO_4 + H_2SO_4$$

Reactions of sulfuric acid with alcohols may have many undesirable characteristics which make them impractical for a sulfuric acid fixing reagent. These characteristics include:

- Reactions proceed best in concentrated sulfuric acid, although sec-butanol acid sulfate formation has been carried out in 60% sulfuric acid (45).
- Excess sulfuric acid is required.
- Many side reactions occur.
- Reaction products, in many cases, are not known.
- Reaction conditions must be carefully controlled.

Oxidation-Reduction Reactions -- Sulfuric acid is not a strong oxidizing agent, the potential for the reaction $H_2SO_4 \rightarrow H_2SO_3$ being only 0.20V. This type of reaction for fixing sulfuric acid in the H_2SO_3 form is not very promising. Sulfuric acid, however, can be fixed as the metal sulfate by active metals which lie above hydrogen in the redox potential series. The following oxidation reduction reaction occurs in this case:

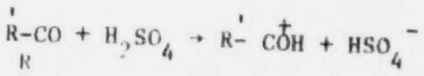
$$\frac{2}{x}M + 2H^+ \rightarrow \frac{2}{x}M^{X+} + H_2(g).$$

Metals which can undergo this type of reaction to produce the metal sulfate salt include aluminum, titanium, zirconium, zinc, chromium, iron, cadmium, cobalt, nickel, tin, lead, manganese, and many of the rare earths. These metals are all possibilities for collecting sulfuric acid by impaction on a foil.

The salts $Ce(SO_4)_2$ and $TlHSO_4$, which decompose at 195 and 120°C, respectively, look particularly interesting. Although metal foils are good candidates for sulfuric acid collection, there are many parameters which should be evaluated experimentally to determine their usefulness. These include:

- Eliminating excess water from the reaction zone by heating the incoming air stream or foil, or both.
- Determining the catalytic effects of the foil for oxidation of SO_2 to SO_3.
- Determining interferences from oxide formation.
- Separating the product of the metal sulfuric reaction from other atmospheric sulfates. This could possibly be accomplished by selective decomposition or selective extraction.

Acid-Base Reactions -- Sulfuric acid is an excellent non-aqueous protonic solvent. In its concentrated form, it is capable of protonating even the weakest organic bases. Organic compounds such as ketones, carboxylic acids, esters, ethers, amines, amides, and even some aromatic hydrocarbons, react with concentrated sulfuric acid to form a protonated complex:



$$\overset{'}{R}\text{-}\underset{R}{C}O + H_2SO_4 \rightarrow R\overset{'}{\text{-}}\,C\overset{+}{O}H + HSO_4^-$$

This ability to protonate and dissolve weak bases is used in organic qualitative analysis schemes to aid in identification of functional groups present. It can also be used for colorimetric quantitative analysis due to the formation of distinctly colored complexes with certain compounds (46,47). In general, these reactions do not occur in dilute sulfuric acid solutions, and are of little interest for a sulfuric acid fixing reagent. The exception to this is the amines. Many organic amines are sufficiently strong bases that they will react with sulfuric acid even in very dilute solutions.

Amines react with aqueous acid solutions to give an amine salts of the types:

$$(RNH_3^+)_2SO_4^=$$

$$(R_2NH_2^+)_2SO_4^=$$

$$(R_3NH^+)_2SO_4^=$$

The reaction is virtually instantaneous. For example, the protonation of trimethylamine has a rate constant of $k = 2.5 \times 10^{10}$ liter mole^{-1} sec^{-1} (48). Assuming that the reaction $(CH_3)_3\dot{N} + H^+ \rightarrow (CH_3)_3NH^+$ is second order, the time required for the H^+ concentration to drop to half its initial value is

$$t_{1/2} = \frac{1}{KC_o}$$

where K is the rate constant and C_o is the initial molar concentration. Using the above equation, droplets of H_2SO_4 over a range of 0.1 to 10 molar concentration would have a half-life of approximately 0.4×10^{-9} to 0.4×10^{-11} seconds. In addition to the reaction rate advantages of acid-base reactions, many of the low molecular weight amines have the added advantage of being highly volatile. Thus, it appears that low molecular weight amines have great potential as gaseous fixing reagents.

Most acid-base indicators are, themselves, weak organic acids that show one color in the acid form and another in the anionic form, i.e.,

H^+In^-	$H^+ + In^-$
(Acid Form, Color A)	(Basic Form, Color B)

These weak acids are frequently prepared in a salt form in order to increase water solubility and enhance the acid's usefulness as an indicator:

$$Na^+In^- \rightarrow Na^+ + In^-$$

Thus, when the salt form is dissolved, it dissociates, and the anion form reacts with the H^+ present to give the characteristic color, dependent upon the pH of the solution. The cation from the salt should then be free to react with the anion of the acid under consideration. Gentle heating of the collection surface during sampling should volatilize water and cause the sulfate salt to form instantaneously. Judicious choice of the cationic portion of the indicator salt should result in the rapid formation of low decomposition temperature metal sulfate salts.

Many of the salt forms of these acids are prepared by simply neutralizing the free acid form with a strong base. For example, the sodium salt of methyl red can be prepared by adding NaOH to an equal amount of the parent methyl red acid. Theoretically, it should be possible to prepare any metal salt by adding the metal's basic form (the hydroxide or oxide) to the acid. This should allow the preparation of a metal salt indicator that can react with the sulfate ion to form a sulfate adduct with a desirable decomposition temperature.

In selecting a possible metal ion for indicator synthesis, several criteria should be considered:

1) The ionization proceeds in two steps:

$$H_2SO_4 \leftrightarrow H^+ + HSO_4^- \qquad k. >> 1$$

$$HSO_4^- \leftrightarrow H^+ + SO_4^= \qquad k = 1.2 \times 10^{-2}$$

Therefore, the primary anionic species present is the hydrogen sulfate ion.

2) The metal hydroxide or oxide must be sufficiently basic to react fairly completely during neutralization of the indicator acid.

3) The resulting sulfate or hydrogen sulfate should have as low a decomposition point as possible.

4) The metal should have a valence state of one or two, as most indicators are monobasic acids.

Thallium (I) appears to fulfill all these criteria. Its basic form, TlOH, is a strong base which should be capable of reacting with an acid indicator. $TlHSO_4$ has a decomposition point of 120°C, with Tl_2SO_4, SO_2 and O_2 as products.

The choice of indicator is much less constricted. The indicator selected should not contain sulfur; thus, any interference from decomposition of the indicator itself is eliminated. A high pH for indicator color change is desirable, as this implies a high pK_{in}, and, therefore, a strong tendency to react with protons and drive the reaction toward release of Tl^+ and HSO_4^-.

The acid-base reaction between H_2SO_4 and the indicator should result in the formation of $TlHSO_4$ which decomposes at a low temperature to give SO_2. Although other acids may react, only sulfur-containing ones could interfere.

Reaction Kinetics Conclusions -- Sulfuric acid reacts with several classes of organic compounds, but only its reactions with amines seems to occur very rapidly. Electrophilic addition and substitution reactions require that the acid be concentrated almost to the point of fuming, since the active agent is really SO_3. When concentrated H_2SO_4 is added to highly branched liquid alkenes, and even highly activated aromatic compounds like phenol, the reaction is imperceptibly slow. Other reactions with organic compounds involving sulfuric acid's oxidizing or dehydrating properties can be duplicated by nitric acid, phosphoric acid, or a mixture of the two.

The reaction of sulfuric acid with organic amines is fundamentally different because it is essentially an acid-base neutralization. The basic amine group accepts a proton readily and acquires its charge, thus becoming the counter-ion to sulfate. If 100% sulfuric acid is used, the solid amine sulfate salt is immediately formed. If more dilute acid contacts the amine, the acid is neutralized, but the salt does not crystallize until the water is evaporated. Thus, it appears that the sample will have to be dried as it is collected to insure immediate fixation. In the case of certain high-molecular weight amines, the sulfate is insoluble in water, so the crystals form immediately, regardless of dilution of the acid. This, again, leads us to the intriguing possibility of using a volatile amine vapor to fix the acid in a gas-phase reaction. Huygen (49) found that flushing a filter containing H_2SO_4 for two minutes with diethylamine vapor was sufficient to complex the H_2SO_4 for a colorimetric determination. This technique, however, does not possess the required sensitivity or selectivity.

SEPARATION OF INTERFERING SPECIES

It is essential to a successful analytical method that the substance which is actually measured be a unique product of sulfuric acid. There does not seem to be any means of satisfying this requirement without incorporating at least part of the H_2SO_4 molecule in the adduct to be measured. The reactions of sulfuric acid are not sufficiently unique in themselves to form a distinct non-incorporative adduct. Specifically, sulfur from the acid must be contained in the adduct if it is to be measurably distinct from other products of the fixing reagent.

There are various sample collection techniques for atmospheric aerosols which do not collect ambient sulfur gases, i.e., filters. In addition, there are analytical methodologies which are specific for sulfur. These options include the use of Teflon filters for sample collection and the use of the Flame Photometric Detector (FPD) for the specific measurement of sulfur. The FPD and other potential measurement techniques are discussed in Appendix B.

The elimination of sulfur gases and non-sulfur bearing species suggests that the most serious analytical interference to be expected in the analysis of fixed ambient H_2SO_4 adducts will be from particulate sulfates. One way of limiting this interference is to form an adduct which will volatilize or decompose at a lower temperature than other particulate sulfates. Table 6, compiled from various sources (50-52), gives the published decomposition temperatures of the more common ambient sulfate particulates. As can be seen from the table, it would be desirable for the H_2SO_4 adduct to have a decomposition temperature of $\sim$200°C or less. The decomposition products of the adduct, particularly SO_2, could then be analyzed using the sulfur specific Flame Photometric Detector. Therefore, if selective deomposition

TABLE 6. DECOMPOSITION TEMPERATURES OF AMBIENT SULFATES (50-52)

Sulfate	Decomposition Temperature, °C
NH_4HSO_4	230
$(NH_4)_2SO_4$	235
$FeSO_4$	255
$Al_2(SO_4)_3$	770
$ZnSO_4$	740
$CdSO_4$	1000
$CoSO_4$	989
$NiSO_4$	840
$SnSO_4$	650
$PbSO_4$	1000
$MnSO_4$	850
$CaSO_4$	1000

is to be considered as a means of eliminating particulate sulfate interference, then the fixing reagent must take on the added requirement that it form an adduct with H_2SO_4 that can be decomposed at a temperature of less than 200°C.

Another possibility is to form an adduct which would selectively precipitate or dissolve in a dry organic reagent in which interfering particulate sulfates undergo the opposite reaction. If the fixing reagent is soluble in an organic solvent, or can be used as the solvent itself, then the sampling procedure is simplified. This technique will probably be most useful for organic adducts, but it may be possible to extract H_2SO_4 fixed in certain acid salts by an organic reagent which would normally react with H_2SO_4. It is felt, as previously stated, that this technique is more problematic than thermal decomposition, due to the hydrolysis of ambient sulfate salts in the presence of water. The present discussion will deal with both types of potential adduct candidates.

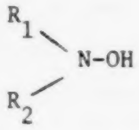
Potential Sulfuric Acid Adduct Classes

Thermal Decomposition -

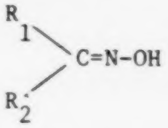
Oxygen and nitrogen in organic compounds are usually sufficiently basic to become protonated by a strong mineral acid. Formation of oxonium salts by protonation of the -OH group usually occurs in alcohols. Concentrated sulfuric acid dissolves in almost any organic compound containing oxygen such as carbonyl compounds, ethers, etc. by the same mechanism. However, these oxonium salts are not sufficiently stable to isolate as such; they are useful only as soluble forms of sulfuric acid in organic solvents.

Organic nitrogen (excluding nitro-, nitroso-, and quaternary ammonium compounds) is more strongly basic than oxygen because its unshared electron pair is more available for protonation due to the lower electronegativity of this element. Consequently, "amine sulfates" are more stable than oxonium sulfates and can be isolated as ionic solids. This can be demonstrated by adding concentrated H_2SO_4 to diethylamine, which produces rapid precipitation of a white solid. Most amine sulfates are soluble and completely ionized in aqueous solution. Hydrolysis of the protonated amine produces a fairly acidic solution, so it would seem desirable to heat the sample collection surface to remove water and form dry amine sulfate crystals. This would not be necessary for an insoluble amine sulfate; however, the thermal stability of these compounds seems to be too high for selective thermal decomposition analysis.

Even water soluble amines seem to be at the limit of selective analyzability. Diethylamine sulfate does decompose slowly at 200°C and releases SO_2 more quickly then ammonium sulfate at the same temperature. Other amine sulfates, however, such as pyridinium sulfate (from pyridine), require a higher temperature at which the inorganic sulfates interfere. For this reason amines and amine-derivatives in which oxygen is bonded to nitrogen : hydroxylamines and oximes:



Hydroxylamine



Oxime

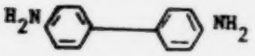
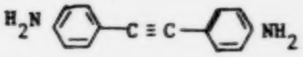
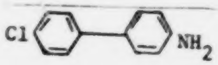
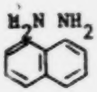
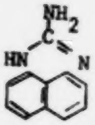
were considered to have the greatest potential, particularly in the use of a gas-phase reagent to fix sulfuric acid as it is collected. The primary effect of oxygen in these compounds is to reduce the base strength of nitrogen. As a result, the corresponding sulfate salts tend to be less stable and decompose at a lower temperature then the basic amine. An analogous difference is observed in the decomposition temperatures of ammonium sulfate and hydroxylamine sulfate:

$(NH_4)_2SO_4$	$(NH_2OH_2)_2SO_4$
240°	180°

Of course, many factors besides base strength are involved in the decomposition temperature, but this seems to be a useful generalization.

Insoluble Sulfates --

Several organic amines have been investigated which are distinguished by the very low solubilities of their sulfate salts in both aqueous and non-aqueous solvents. These compounds are listed below:

Compound	Formula	Solubility of Sulfate, g/l
Benzidine (53)		0.098 (25°C)
4,4'-diaminotolane (53)		0.059 (25°C)
2-amino-4'-chlorodiphenyl (54)		0.155 (25°C)
1,8-diaminonaphthalene (55)		0.222 (25°C)
2-aminoperimidine (55) perimidylammonium bromide (56)		0.020 (18°C)

These reagents at first appear to be promising candidates for fixation of sulfuric acid, both because they react with dilute acid and because they are extremely insoluble. The latter infers that the selective solubility of interfering species would serve as a means of separation prior to the analysis of the sulfuric acid adduct. However, it appears likely that the amount of sulfuric acid adduct and interfering sulfates collected during any reasonable collection period would be so small that solubility differences between the various species would be ineffectual as a means of separation. For example, the solubility of the most insoluble sulfate known, perimidylammonium sulfate, is 0.020 g/l. This corresponds to a solubility of 20 μg/cc or for a 10 cc extraction volume, a total of 200 μg of perimidylammonium sulfate would be soluble. Considering that the sulfuric acid aerosol lower concentration of interest to this program is 0.25 $\mu g/m^3$, a sample volume of 200 m^3 would be required to exceed its solubility limit. Thus, at a typical aerosol sampling rate of 14 l/min, it would take approximately 240 hours to sample a sufficient volume to exceed the solubility of perimidylammonium sulfate. It would, therefore, appear that even for the most insoluble sulfate known, selective solubility is not an attractive approach.

SUMMARY OF THEORETICAL DEVELOPMENT

Sulfuric acid is a highly reactive species of significant environmental importance. The advent of the automobile catalytic converter and the use of high sulfur fuels will cause the level of sulfuric acid aerosol in the environment to increase in the future. Sulfuric acid aerosols are believed to exist in concentrations of 0.25 to 50 $\mu g/m^3$ with an aerosol particle diameter of 0.02 to 2.0 μm. Both the aerosol droplet size distribution and the concentration of acid in the droplet are related to environmental variables such as temperature and relative humidity.

The precise health implications of current levels of ambient sulfuric acid aerosols are the basis for much scientific speculation at this time. This speculation is due, in part, to difficulties in measuring existing sulfuric acid aerosol concentrations. These difficulties are associated with an inability to measure sulfuric acid in the presence of interfering sulfates and an inability to prevent artifact formation during aerosol sample collection. It appears that these difficulties might be resolved by reacting the acid during collection to form an adduct which can be selectively analyzed in the presence of interfering sulfates.

Sulfuric acid aerosols can be collected for analysis by a variety of techniques. Filtration techniques using Mitex LS filters offer the advantage of efficiently sampling particulates of various sizes, being inert, and relatively simple to apply. Other aerosol collection techniques, such as precipitation and impaction collection methods, are often expensive and difficult to utilize.

It appeared that aerosol adduct formation could best be accomplished by utilizing reagents which are sufficiently volatile that they can be used in the gas phase during sample collection. Gas phase fixation offers the advantage of being able to continuously supply fresh reagent to a moving sample stream prior to actual sample collection. The primary requirement in the formation of sulfuric acid adducts is that the reaction between the acid aerosol and reagent be sufficiently rapid to prevent artifact formation on the collection surface. An examiantion of the reaction classes of sulfuric acid suggests that only acid-base reactions are sufficiently rapid to satisfy the kinetics requirement. Volatile organic amines appear to offer the advantage of both gas phase fixation and the rapid kinetics of acid-base reactions. Calculations (Appendix B) based on a model consisting of several volatile organic amines in a gas flow reactor system indicate that this approach for fixing sulfuric acid aerosols is theoretically feasible.

There are many analytical techniques available that show potential for the analysis of sulfuric acid adducts. Since it is desirable to incorporate the sulfur from the sulfuric acid aerosol into the adduct molecule, a technique which is both selective and sensitive for sulfur would have obvious advantages. The Flame Photometric Detector (FPD) fulfills this requirement, as it responds primarily to sulfur (374 nm) and is sensitive to sulfur at the nanogram level. Thus, the FPD would eliminate all interferences except those which contain sulfur. Sulfur-containing gases should not interfere, since they would probably pass through the collection filter. It is possible, however, that some sulfur gases might react with the fixing reagent and subsequently be collected on the filter surface.

The use of the FPD as the analytical detection method suggests that the major interfering species would be ambient particulate sulfur compounds. There are two methods which might be utilized to eliminate these interfering species: selective solubility and thermal volatilization/decomposition. Selective solubility appears to be the least promising approach because of the low levels of acid aerosol anticipated in collected samples. The literature suggests that most anticipated environmental sulfur-containing particulates would decompose well above 200°C. Thus, the selective analysis of the adduct in the presence of other sulfur-containing species has the greatest potential for success if an adduct can be defined which volatilizes/docomposes below 200°C.

The preceding discussion has attempted to illustrate the theoretical manner in which the proposed method evolved from the main possibilities for fixation, sampling, and analysis of sulfuric acid aerosol. Rapid formation of the adduct and convenience of sampling required a gaseous amine or amine-derivative fixing reagent. Considerations of selective analysis added the requirement that the adduct decompose at <200°C by releasing a sulfur gas. The following sections describe the experimental approach, the experimental work and the results of the evaluation of the proposed approach for the analysis of ambient sulfuric acid aerosols.

SYNOPSIS OF PROPOSED METHOD

1) An aerosol sample is first drawn into a glass tube and then through a Teflon filter by a vacuum pump. Simultaneously a gaseous organic compound containing reduced nitrogen (amine, hydroxylamine, or oxime) is added to the glass tube through sideports. Sulfuric acid in the sample is thus fixed as a stable adduct (the sulfate or hydrogen sulfate salt of the fixing reagent), and collected on the filter.

2) The sample is analyzed by heating the filter to a distinct temperature (200°C) in a closed cell with non-reactive surfaces. After five minutes, an inert carrier gas is used to flush the sulfur dioxide evolved from the sample into a flame photometric detector (FPD). The FPD may be calibrated by injecting known SO_2 gaseous solutions or by preparing known H_2SO_4 standards. Alternatively, the decomposition gases can be continuously purged into a West-Gaeke Bubbler and analyzed selectively for SO_2. The absorbance of the solution is measured at 560 mu and the concentration of evolved SO_2 determined from a calibration generated from sodium bisulfite standards.

3) Only compounds containing sulfur are detected by the FPD, while the West-Gaeke technique determines only SO_2. Sulfate salts, including $(NH_4)_2SO_4$ and NH_4HSO_4, do not interfere because they do not decompose significantly at 200°C. Sulfur gases, primarily SO_2, may be absorbed by the fixing reagent and collected on the filter, but the compound thus formed can be selectively removed from the sample by decomposition at 100°C. Finally, fixation of the acid as it is collected reduces its acidity and decreases the probability of reaction with other substances on the filter.

SECTION 5

EXPERIMENTAL

AEROSOL GENERATION

The main requirement for evaluating any analytical methodology is the availability of satisfactory standards. These standards must not only contain known amounts of the species of interest, but they must also simulate actual sample matrices. Once the proposed methodology is evaluated using standards which conform to the above requirements, the technique can be used with a known degree of confidence on actual samples.

The investigation of methods proposed for the analysis of ambient sulfuric acid aerosols was a particularly difficult problem, since there was much speculation about their actual size distribution in the environment. Mirabel and Katz (26) predicted that ambient conditions such as temperature and relative humidity greatly influence aerosol growth rates and the concentration of sulfuric acid within individual droplets. There appears, however, to be two primary size ranges of sulfuric acid aerosols emerging which are thought to be representative of the environment: aerosols in the 0.01 to 0.1 μm size range and those in the 0.1 to 3.5 μm size range (27). Thus, any attempt to evaluate an analytical methodology for the analysis of sulfuric acid aerosols must incorporate known standards in the size range from approximately 0.01 to 3.5 μm.

A review of the literature pertaining to aerosol generation techniques suggested that there was no singular technique that could be used to generate aerosol droplets over the entire range of interest to this research. Therefore, two aerosol generators were used during this research: one covering the size range from approximately 0.01 to 0.1 μm, and the other from 0.1 to 3.5 μm.

It was found experimentally that the generation of a known quantitative sulfuric acid aerosol based upon mass balance calculations was not easily obtainable within the scope of this research. These findings were not surprising since the complex relationship between aerosol droplet size, humidity, temperature and aerosol droplet-sulfuric acid concentration had previously been predicted by other investigators (26). Alternative methods of standardizing the aerosol generators for the purpose of closing the mass balance also generally proved inadequate because of the lack of a viable referee method to measure the small amounts of acid aerosol generated. The aerosol generators, however, proved adequate for the deposition of 0.5 to 5.0 μg of sulfuric acid aerosol which was anticipated in environmental samples. Micropipets were routinely used to deliver known amounts of sulfuric acid to filters during the course of this research for precise quantitative determinations. Each of the sample generation techniques is described below.

Thomas Aerosol Generator (0.005 to 0.3 μm droplets)

The sulfuric acid aerosol generator used in the initial experiments was based upon the atomizer-burner model described by Thomas, et al. (40). In this model, a dilute H_2SO_4 solution was aspirated into an H_2-O_2 flame, where it decomposed to H_2O and SO_3. Recombination occurred to yield sulfuric acid aerosol. The rationale for using this type of generator was that it approximated the process by which H_2SO_4 aerosol is thought to be formed in industrial or automotive combustion.

The Thomas generator, illustrated in Figure 8, consisted of a Beckman 4060 Large Bore Atomizer Burner Assembly mounted at the base of a glass stack 1.2 M high by 15.2 cm O.D. Burner gas back-pressures were set at 10.3 mm positive pressure for H_2 and 517 mm positive pressure for O_2. The aspirated solution varied from 0.01N to 1.0N, depending upon the experiment, with a typical delivery rate of 2 ml per minute into the burner jet. Barrett, et al. (57) measured the aerosol distribution of an identical system and found that 98% of the aerosol droplets were between 0.005 and 0.3 μm.

It was thought that the problem of closing the mass balance on this generator was associated with the stack being open at the bottom, which resulted in varying amounts of diluent gas (ambient air) being drawn into the stack. In addition, the aerosol temperature could vary greatly, depending upon room conditions. This generator varied quantitatively by as much as three orders of magnitude, based upon supposedly identical samples.

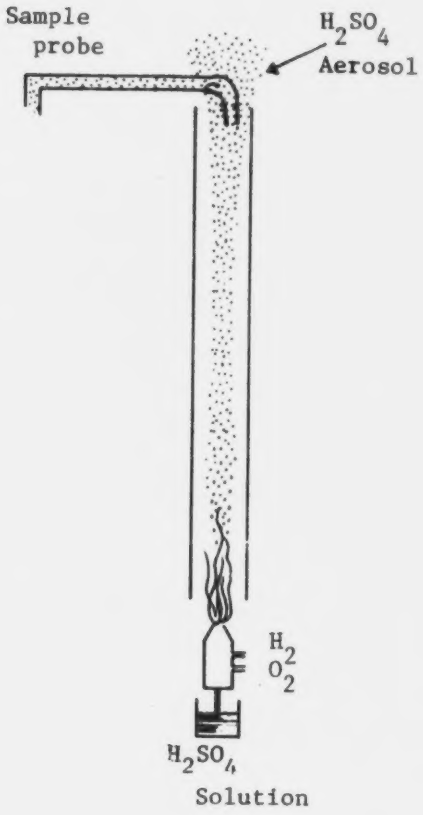


Figure 8. Thomas aerosol generator.

Baird Aerosol Generator (1.0 to 3.0 μm droplets)

The Baird Aerosol Generator illustrated in Figure 9 was a closed system allowing diluent air to be accurately determined. It was constructed from a nebulizer designed for use with the Baird-Atomic D.B.-2 flame photometer, a Fisher burner with concentric glass chimneys, and a large reflux condenser which was approximately 1.2 m long with an outside diameter of 8.8 cm. In operation, a dilute sulfuric acid solution was passed through the nebulizer and aerosol droplets formed. Droplets larger than 3.0 μm strike the nebulizer housing wall and are collected in a "U" trap at the bottom. Aerosol droplets smaller than 3.0 μm do not collide with the housing wall and are transported up the condenser stack to the collection filter. The condenser acts as a stack, mixer and constant temperature bath.

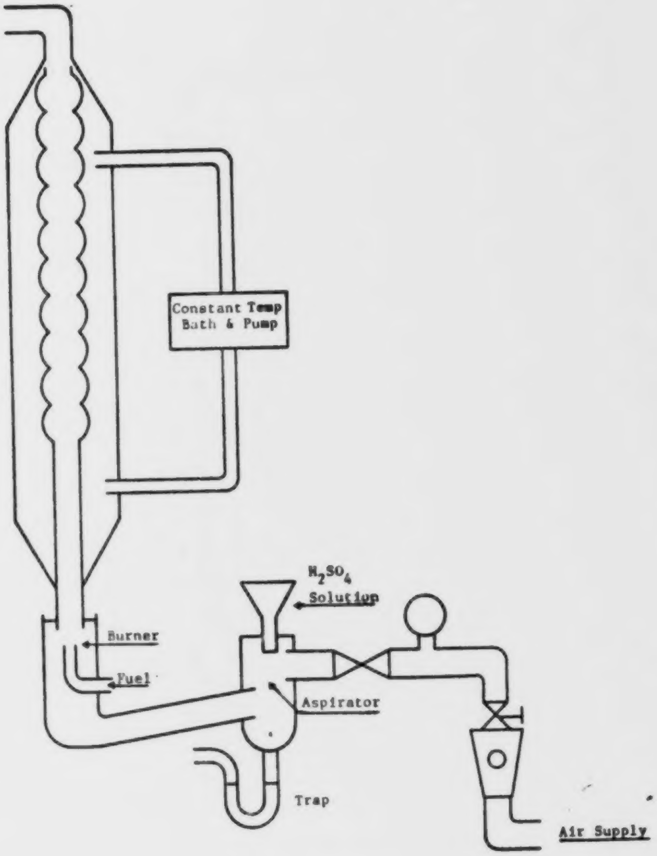


Figure 9. Baird aerosol generator.

The generator was found to operate satisfactorily from 414 to 776 mm positive pressure, delivering 34 l/min of air at the lower value which was normally used for experimental purposes. During a typical run of 30 minutes, 50 ml of sulfuric acid solution was passed through the nebulizer, 48 ml of which was collected in the return trap of the nebulizer. Typically, acid solutions of 0.01 N to 1.0N were used, depending upon the experiment. The Baird generator was found to be reproducible within 20%, but attempts to close a mass balance based upon the amount of acid solution consumed proved impossible. Raabés (58) determined that the size range of the aerosol generated by the Baird nebulizer under similar conditions was 1 to 3 μm.

Micropipet Delivery

Initial experimental difficulties in closing the mass balance between the acid consumed by the aerosol generators and the acid collected on filters necessitated the use of an alternative approach for depositing a known amount of acid onto filters. Basically, this procedure consisted of accurately depositing 10 to 15 μl of sulfuric acid solution onto the surface of a filter media by micropipet. The sulfuric acid solution concentration varied between 0.01N and 1.0N, resulting in depositions of up to 600 μg H_2SO_4 on the filters. This technique proved to be reproducible to within 10% for depositing known amounts of H_2SO_4 onto filters.

AEROSOL COLLECTION AND ADDUCT FORMATION

A Pyrex sample probe (2.5 cm I.D.) was positioned at the top of the Baird aerosol generator and attached by a 35/25 ball and socket joint. The total aerosol stream was drawn through Mitex filters at a flow rate of approximately 34 l/min using a Gast pump as the vacuum source. Isokinetic sampling was maintained by carefully adjusting the sample vacuum source until the nebulizer trap maintained an equal height in both legs, indicating sample input equaled sample output.

A Pyrex sample probe (2.5 cm I.D.) which extended 12.7 cm below the top of the Pyrex aerosol generator stack was used to collect samples from the Thomas generator. The probe was held in place with laboratory clamps after it was found that its location was crucial in determining the size of sample collected. No attempt was made to maintain isokinetic sampling conditions, since the aerosol generator was open at both ends. The sample collection flow rate was approximately 15 l/min when the Thomas generator was used as the source of aerosols. The acid aerosol was drawn through Mitex filters with a Gast pump serving as the vacuum source.

The complete fixing-sample collection system generally used with both aerosol generators is illustrated in Figure 10. Approximately 5 cm of 2.5 cm I.D. Pyrex tubing directed the H_2SO_4 aerosol from the sample probe to a double-neck joint which was attached to the above tube using 24/40 ground glass taper joints. The fixing chamber was attached to the straight-through branch of the double-neck joint, while the 45 degree branch served as the

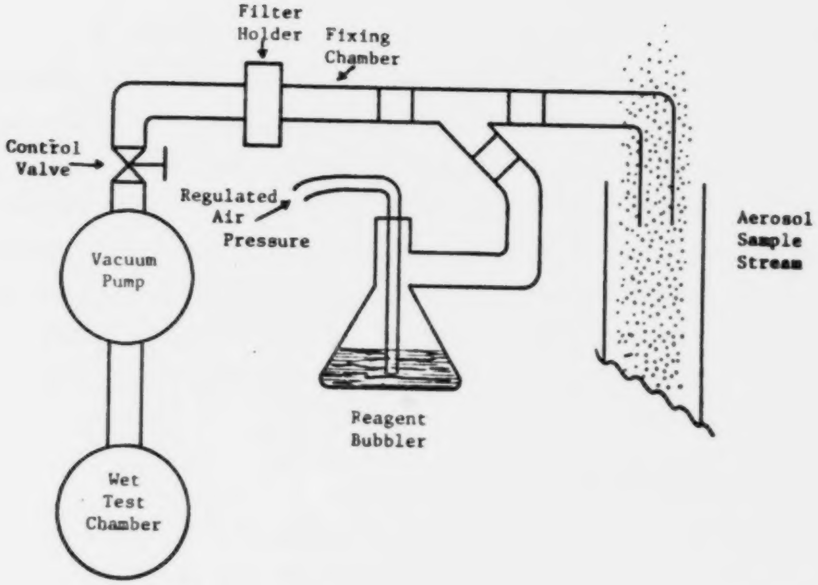


Figure 10. Sample and fixation apparatus.

inlet for the various reagents or interferences. The double-neck joint allowed for the simultaneous addition of both acid aerosol and fixing reagent into the reaction chamber. The fixing chamber consisted of a 20.3 cm length of 2.54 cm I.D. Pyrex tubing with a male and female 24/40 ground-glass joint. At the other end of the fixing chamber, a nylon filter holder was attached which held the Mitex LS 5 μm filters for collection of the H_2SO_4 aerosol and adducts. A Gast pump was used to draw the sample stream through the Mitex filters with the pump exhaust being fed into a Precision Scientific Wet Test Meter which accurately measured the total sample volume. Sample flow rate was controlled by the use of a valve located between the filter holder and pump.

A second sampling system was also utilized in which the temperature of the incoming aerosol gas streams could be elevated. This was done in order to study the effect of collecting aerosols at elevated temperatures and to determine if unfixed H_2SO_4 aerosol could be volatilized and efficiently passed through a prefilter.

The device, shown in Figure 11, consists of a 30 cm x 1.8 cm I.D. heavy wall Teflon tube heated by glass-backed tape. The end of the 30 cm heated

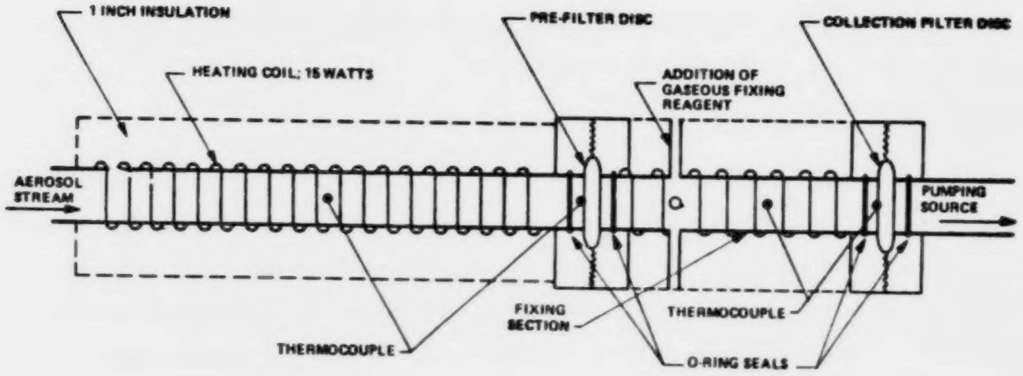

1 INCH INSULATION
PRE-FILTER DISC
COLLECTION FILTER DISC
HEATING COIL; 15 WATTS
ADDITION OF GASEOUS FIXING REAGENT
AEROSOL STREAM
PUMPING SOURCE
FIXING SECTION
THERMOCOUPLE
THERMOCOUPLE
O-RING SEALS

Figure 11. Modified aerosol collection system.

section can be used with or without a Mitex Teflon prefilter which allows the volatilized acid to pass while collecting the remaining particles. Once through the prefilter, the volatilized acid is mixed with fixing reagent in a 15 cm Teflon mixing chamber. The adduct is then collected on a second Teflon filter at the end of the 15 cm section. The fixing chamber is wrapped with a glass-backed heating tape and insulated in order to accurately control temperature. The temperature range over which the sampler operated was from ambient up to ≈200°C.

All aerosol samples, using both collection systems, were generally collected over a period of 2 to 30 minutes, depending upon the concentration of the aspirating solution and the method of aerosol generation. Total volume sampled as measured by the wet test meter was typically 0.03 to 0.95 m^3. Aerosol sample collection flow rates were approximately 15 l/min with the atomizer-burner generator and 34 l/min with the Baird generator.

Fixing reagent vapor, as shown in Figure 11, was generated from a bubbler and delivered to the entrance of the reaction chamber. The bubbler consisted of a 50 ml Erlenmeyer flask with a reagent level of approximately 2 cm. The flow rate through the bubbler was normally held at 0.5 l/min. Theoretical considerations (Appendix A) predicted the approximate concentration of various candidate reagents in both the reagent gas stream and the aerosol sample stream. Heating tape was used to maintain the temperature of the reagents at room temperature and prevent gross concentration changes caused by solution temperature fluctuation.

ANALYSIS OF SAMPLES

Two types of samples were subjected to various analytical methodologies during this investigation. One type of sample consisted of those prepared using the aerosol generators or pipet delivery method and were normally analyzed by a combination of thermal decomposition and sensitive analytical techniques. These determinations served to indicate the usefulness of the proposed methodology under simulated field conditions. The second type of sample consisted of those prepared in larger quantities in order to obtain additional information about a specific area of the proposed methodology.

Decomposition Apparatus

The device constructed to analyze the adducts consisted basically of a heated cell to thermally decompose the sample, and a three-way valve arrangement by which a helium purge gas could be used to deliver the decomposition products to the analytical detector. Normally, the analytical detection was accomplished by use of a Flame Photometric Detector (FPD) or the West-Gaeke (59) technique for the determination of SO_2. Figure 12 is a sketch of the sample decompositon chamber. The heating tube (19 cm long x 1 cm diameter) is constructed of Teflon and is surrounded by a large mass of aluminum to reduce temperature fluctuations. The aluminum housing also serves to maintain an even temperature profile across the cell's length. The O-ring seals are outside of the heated zone to eliminate the degradation problem associated with the O-rings in the original prototype.

Flame Photometric Detector (FPD)

The FPD used in this investigation was a Melpar Model 100 integrated with the electrometer of a Hewlett Packard 5750 gas chromatograph. Typical electrometer settings during this research were on a range setting of 10 and an attenuation of 32, which resulted in a detection sensitivity of approximately 10^{-10} amps. Basically, the decomposition gases were simply purged through the FPD at 60 cc/min with the aid of helium carrier.

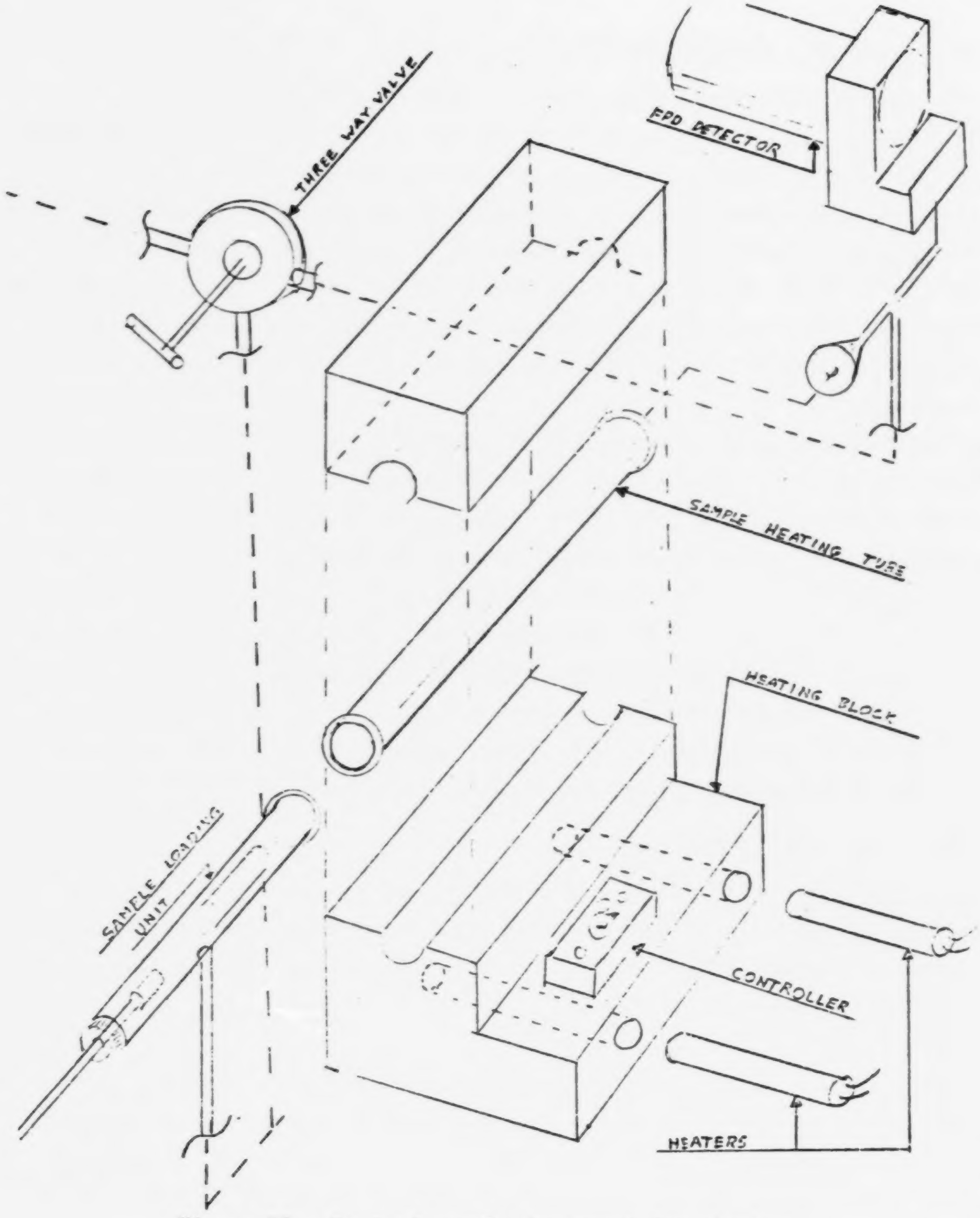

THREE WAY VALVE
EPD DETECTOR
SAMPLE HEATING TUBE
HEATING BLOCK
SAMPLE LOADING UNIT
CONTROLLER
HEATERS

Figure 12. Revised sample decomposition chamber.

West-Gaeke SO_2 Analysis Technique

The West-Gaeke technique (59) is used for the analysis of SO_2. In this method, SO_2 is collected in an aqueous solution of 0.1 M sodium tetrachloromercurate where it is fixed as the stable disulfitomercurate (II) ion. When a p-rosaniline hydrochloride-hydrochloric acid mixture and formaldehyde are added, a violet color is produced proportional to the amount of fixed SO_2 present. The absorption maximum at 560 mμ is used for a spectrophotometric measurement. This method will detect the equivalent of 1 μg H_2SO_4 converted to SO_2 and dissolved in a 10 ml collection solution.

Basically, use of the West-Gaeke technique consisted of preparing samples on Mitex filters using the aerosol generator or by pipet. These samples were then heated to 200°C individually in the sample decomposition cell and the evolved gases bubbled into 10 ml of the collecting solution with a helium carrier gas. After collecting for 15 minutes, the solution was treated with 2 ml 0.2% formaldehyde and 5 ml of 0.04% acid bleached p-rosaniline dye. After allowing 30 min for the color to develop, the absorbancy at 560 mμ was compared to that of a curve prepared by using standard solutions of sodium bisulfite in sodium tetrachloromercurate. A Beckman DK spectrophotometer was used to measure the absorbance.

Supporting Instrumental Analysis

Analytical methods other than the FPD and the West-Gaeke technique were used to obtain additional information concerning adduct decomposition. These techniques, however, were not considered adequate for the analysis of actual environmental samples.

Differential Thermal Analysis (DTA) - DTA was used to obtain information about the temperatures at which candidate adducts and potential interfering substances decomposed. An Aminco Model 442 was used for the purposes of this investigation. Generally, samples were prepared for differential thermal analysis by mixing H_2SO_4 solution and adduct forming reagent together in a ratio of approximately 1:2. The samples were then purified by conventional laboratory techniques such as filtration.

Mass Spectrometry - Mass spectrometry was utilized to identify the gases released by decomposing adducts. All of the adducts examined were found to release SO_2 at 200°C, but no detectable SO_3. There was some ambiguity in these results, however, because even unreacted H_2SO_4 gave predominantly SO_2 at this temperature. Generally, samples subjected to mass spectrometric analysis were prepared by gas phase fixation utilizing the aerosol generators and subsequent collection on Mitex LS filters. The filters were inserted into a sealed 0.95 cm O.D. Pyrex tube which was then attached to the mass spectrometer inlet with a glass stopcock. The sealed vial was then evacuated and the stopcock opened to allow the decomposition gases to enter the mass spectrometer. The sealed tube was slowly heated to 200°C and a light oscilliograph used to record the spectra generated. An EAI Model 250 quadrapole mass spectrometer was used for these studies.

Infrared Spectroscopy - A Beckman Acculab-6 infrared spectrometer was used on several adducts to obtain structural information indicating that the products were the result of an acid-base reaction. Typically, samples were prepared by allowing equal volumes of H_2SO_4 solution and fixing reagent to react in miniature reaction vials (1 ml). The products were then subjected to various clean-up procedures and applied to KBr salt crystals for analysis.

Ammonia Specific Ion Electrode - An Orion Model 95-10 ammonia electrode was used to investigate the reactivity of ammonia with H_2SO_4 aerosol and several of the adduct candidates. Basically, these experiments involved forming and collecting the various adducts in the usual manner with the aerosol generators, and subsequently exposing them in place to a dynamic ammonia environment of 250 ppm. The samples were then removed from the collection device and placed in 100 mls of deionized water. One ml of 10 molar sodium hydroxide was then added to the solution to generate NH_3, which was detected by the ammonia specific ion electrode. The amount of NH_3 generated was indicative of the reactivity of each adduct with NH_3.

Heilige Turbidimeter - A Heilige Model 8000-TS Turbidimeter was used for analysis of sulfate (sulfuric acid or sulfate adduct) deposited on filters by micropipet. The filters were placed in 50 ml of deionized water. Ten milliliters of a sodium chloride-hydrochloric acid solution were then added, followed by 0.29 grams of solid barium chloride which was used to form the precipitate barium sulfate. The mixture was then stirred using a magnetic stirrer for five minutes, placed in the appropriate turbidimeter tube and the amount of sulfate present determined by correlating the turbidimeter reading to a standard graph of known $SO_4^=$ versus the turbidimetry reading.

Dräger Tubes - Dräger tubes were used to approximate the concentration of ammonia in the gas streams passing through collection filters during adduct interference studies. Dräger tubes consist of 15.2 cm x 0.95 cm O.D. glass tubing packed with a solid material. The solid material is impregnated with a chemical that changes color as a gas containing NH_3 is passed through it. The length of discoloration as measured by a calibration scale on each tube, is indicative of the concentration of NH_3 in the gas stream. The tubes are accurate to ± 20% of the measured value. Measurements were made by passing a known volume of the interference gas stream through the Dräger tube immediately after the filter holder containing a blank filter.

SECTION 6

RESULTS AND DISCUSSION

PRELIMINARY EXPERIMENTS

Preliminary experiments were initiated at the onset of this research to substantiate the theoretical assumptions from which the proposed approach evolved. These studies were to obtain information in the following areas:

- Verify the decomposition temperatures of common sulfates thought to have relatively low decomposition temperatures.
- Establish preliminary evidence as to the nature of the sulfuric acid/reagent reaction and the products formed.
- Establish the decomposition temperature of various sulfuric acid adducts.
- Establish the operating parameters and sensitivity of the Flame Photometric Detector (FPD) for both unfixed sulfuric acid and SO_2.
- Calibrate the Flame Photometric Detector to establish that the aerosol generators will deposit sulfuric acid in the range of environmental importance.

Decomposition of Sulfate Particulates

Differential Thermal Analysis (DTA) was used to obtain preliminary information about the temperatures at which potential interfering sulfates decompose. Figure 13 is a composite DTA recording of several common sulfates which have relatively low decomposition temperatures. All are above 200°C, except for the melting (sharp peak) of $KHSO_4$ at 180°C, and a slight decomposition of $CuSO_4$ at 200°C. More importantly, ammonium sulfate and ammonium hydrogen sulfate are stable to 250°C and 230°C, respectively. This indicates that an adduct which decomposes and releases SO_2 at 200°C may be analyzed without interference from these substances. All samples were taken from laboratory reagent bottles and ground to a powder prior to analysis.

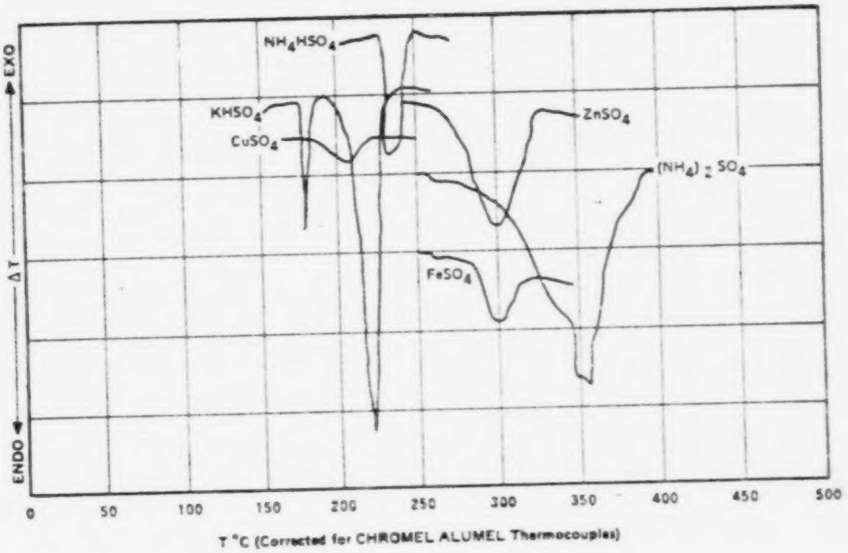


Figure 13. Composite DTA of potential interferences.

Fixing Reagent Reactions

The fixing reagents proposed in this research have been described as volatile amines and amine-derivatives (hydroxylamines and oximes). One compound in each category was evaluated, preliminarily, although this is not to imply that the compound chosen was necessarily the most desirable one. The compounds were:

$(C_2H_5)_2NH$	$(C_2H_5)_2NOH$	$CH_3CH{=}NOH$
Diethylamine (DEA)	Diethylhydroxylamine (DEHA)	Acetaldoxime (AAO)

All are liquids at room temperature, but have sufficient vapor pressure to generate a substantial vapor from a bubbler.

The functional groups of the compounds DEA, DEHA, and AAO are all sufficiently basic to form the bisulfate salt from sulfuric acid. Base strength decreases in the order: DEA > DEHA > AAO. When concentrated H_2SO_4 was added to excess DEA or AAO, white crystals immediately formed and crystallized out of solution. They were water-soluble and turned black (decomposed) when heated. These physical properties, as well as IR spectral evidence, strongly suggested an ionic sulfate or bisulfate salt. DEHA formed a very viscous yellow oil when H_2SO_4 was added, but this oil was also water-soluble and decomposed when heated. A peak at 1650 cm^{-1} in the IR spectra of both the DEHA and AAO adducts (Figures 14 and 15, respectively) was absent in the unreacted reagent and acid. This suggested an N-H bending vibration from protonation of nitrogen, as postulated in the formation of the bisulfate. The product of the reaction between DEA and H_2SO_4 was previously shown by Huygen (49) to be diethylamine sulfate.

Thus, it appeared that these compounds do react with sulfuric acid by proton transfer, forming a sulfate of bisulfate salt. There was no reason to suppose that the product would be different when formed under sampling conditions.

Adduct Decomposition in DTA Apparatus

DTA was used as a preliminary means of establishing the temperature at which the various adducts decomposed. DTA of the products obtained from the reaction of H_2SO_4 with DEA, DEHA and AAO showed that a decomposition occurred below 200°C in each case. Release of a sulfur gas at 200°C was then confirmed for all three adducts by heating in the decomposition chamber and purging the gases into the FPD. Mass spectra indicated that SO_2 was the main gas, and this was supported by the West-Gaeke bubbler (which does not detect SO_3 or SO_4^{-2}).

Several other amine sulfates were also examined by DTA: perimidylammonium sulfate (an insoluble salt) and pyridinium sulfate (from pyridine). The DTA, as shown in Figure 16, indicated that no decomposition occurred under 250°C. Consequently, these two species were not considered desirable as sulfuric acid adducts.

Flame Photometric Detector (FPD)

In order to insure that the amount of H_2SO_4 aerosol being deposited on filters by the aerosol generator was in the quantitative range anticipated in actual environmental samples, it was necessary as a preliminary step to determine the approximate amount of acid being deposited. This was accomplished by comparing the response characteristics of the FPD for both H_2SO_4 aerosol

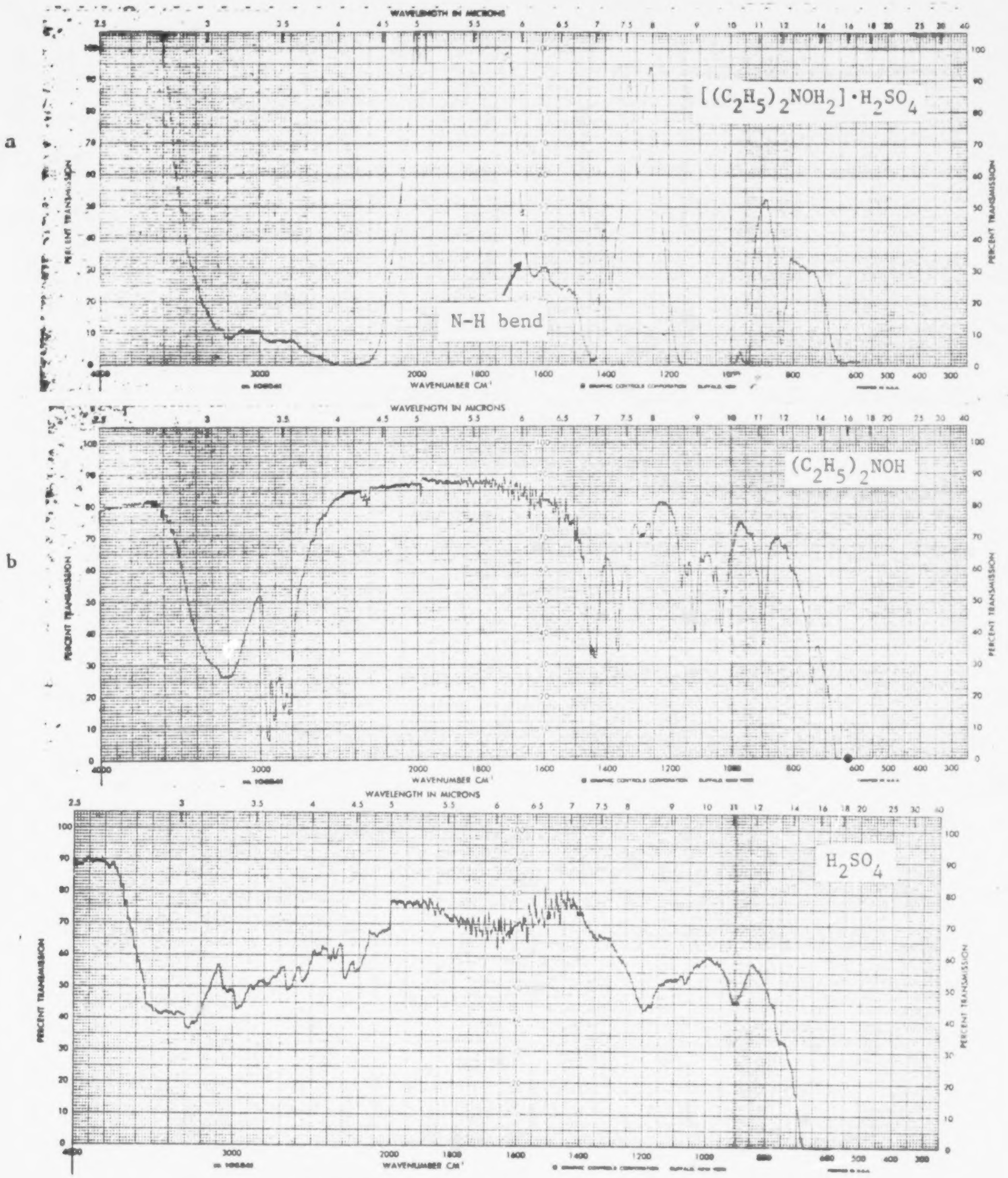


Figure 14. IR spectrum of a) diethylhydroxylamine sulfate, b) diethylhydroxylamine and c) sulfuric acid.

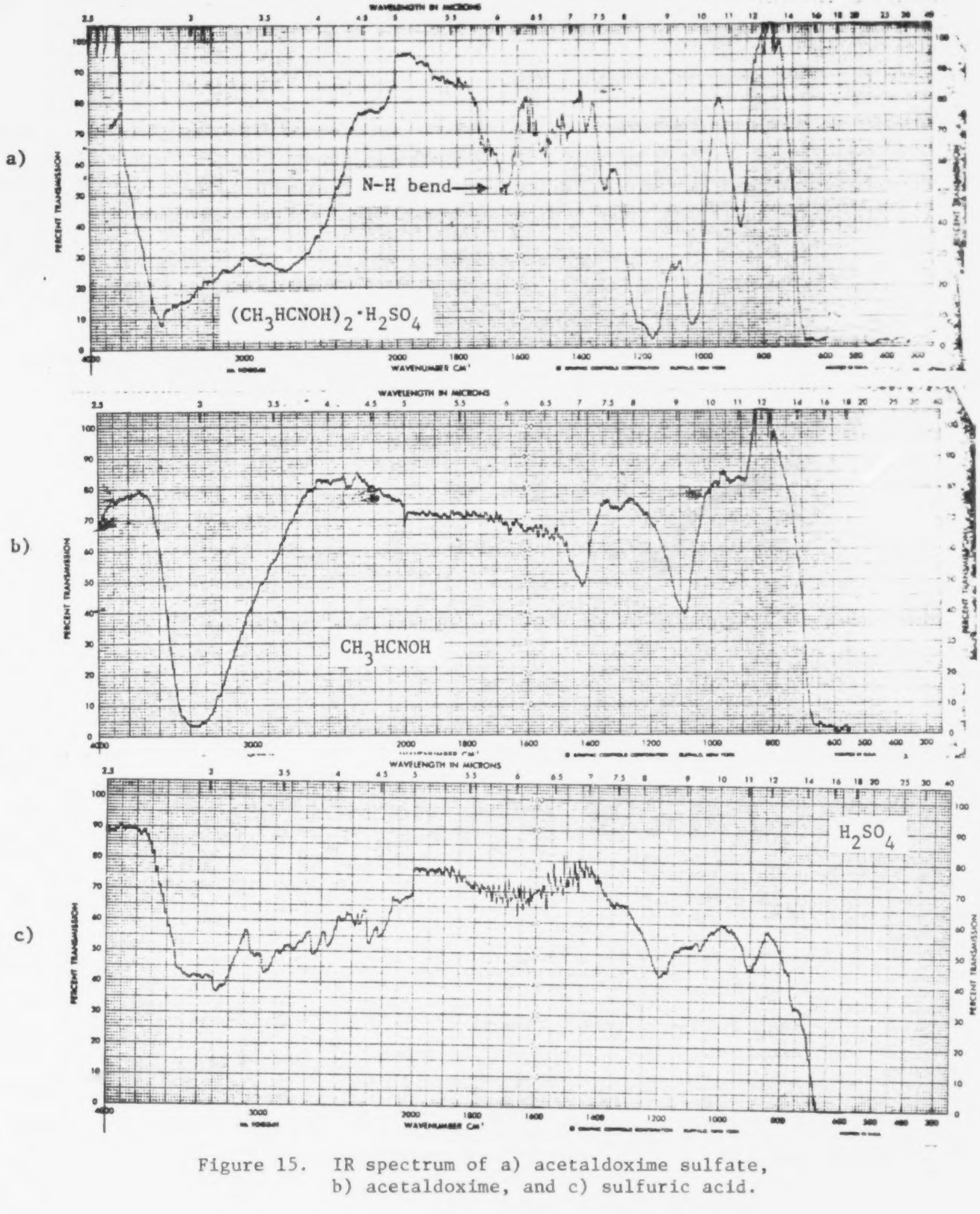


Figure 15. IR spectrum of a) acetaldoxime sulfate, b) acetaldoxime, and c) sulfuric acid.

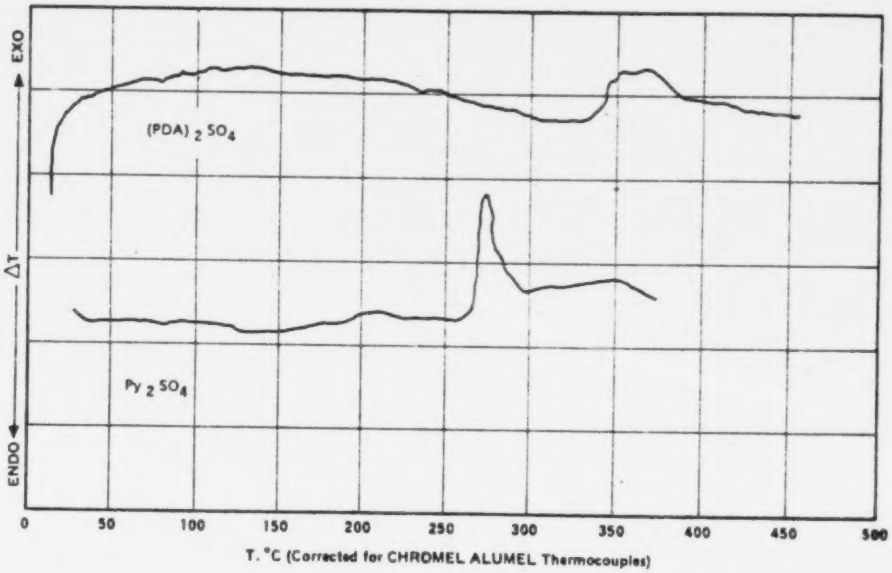


Figure 16. $(PDA)_2SO_4$ and Py_2SO_4 DTA.

as collected from the aerosol generator to the FPD response of known quantities of SO_2. The amount of H_2SO_4 aerosol anticipated in environmental samples is in the range of 0.05 to 5.0 μg, depending upon sample collection time.

Initially, when samples from the aerosol generator were run through the FPD after being volatilized in the decomposition chamber, very peculiar recordings were obtained. The main peak was extremely broad, requiring several hours to tail to baseline, and was often preceded by a small sharp peak. Figure 17 illustrates some of these recordings. It was suspected that these recordings were artifacts of a saturated detector. As a result, several experiments were carried out with known SO_2-air mixtures to clarify the response characteristics of the FPD.

For these experiments, the sample cell was removed and the carrier line was connected directly to the detector inlet. A silicon rubber septum was inserted in the line for injecting SO_2 with a syringe. The source of SO_2 was a compressed-gas lecture bottle, fitted with a valve and a silicon rubber septum. Dilutions of SO_2 in air were carried out in a 305 cc siliclad-coated glass vessel fitted with a rubber septum. Two syringes with Teflon pressure-lock valves were used, with maximum volumes of 100 μl and 500 μl.

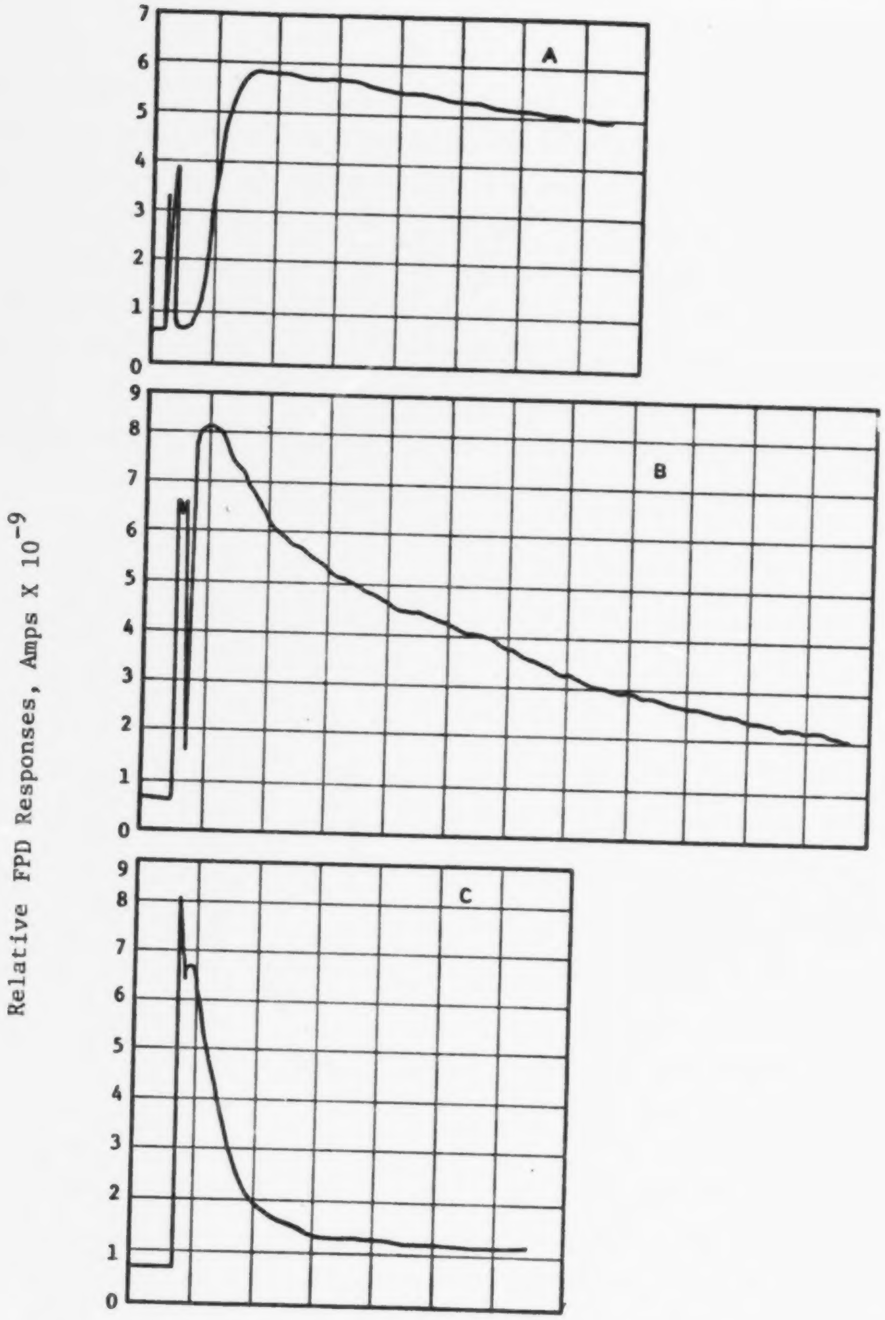


Figure 17. Early FPD recordings from samples.

Several blank injections were made after each sample injection to insure that the syringes were clean of residual SO_2.

Microliter amounts of pure SO_2 from a gas cylinder were injected in the first experiments. Figure 18 shows the effect of injecting progressively larger volumes of SO_2. There was a slight increase in peak width and in separation between the two peaks, but these were not proportional to changes in the SO_2 level. It was apparent that all of these peaks were resulting from a saturated detector. When these peak heights were compared to those previously obtained from samples (Figure 17), it was evident that the aerosol samples had been saturating the detector. It was determined that the delay between the first sharp peak and the second broad one was due to signal suppression by excess sulfur atoms in the flame reabsorbing the emitted light.

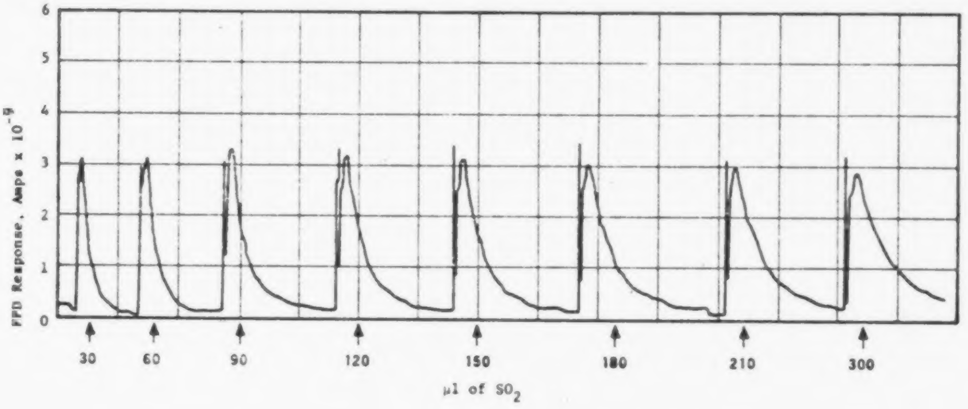


Figure 18. Effect of injecting progressively larger SO_2 volumes.

In order to bring the sample size down to the quantitative response range, various dilutions of SO_2 were made. When microliter volumes of these dilutions were injected, the peaks were much sharper and their heights were related to the amount injected as Figures 19 and 20 show. There was some difference observed between the two syringes in Figure 20, the smaller one producing less response from the same volume of sample. This was possibly due to the greater surface area-to-volume ratio of the smaller

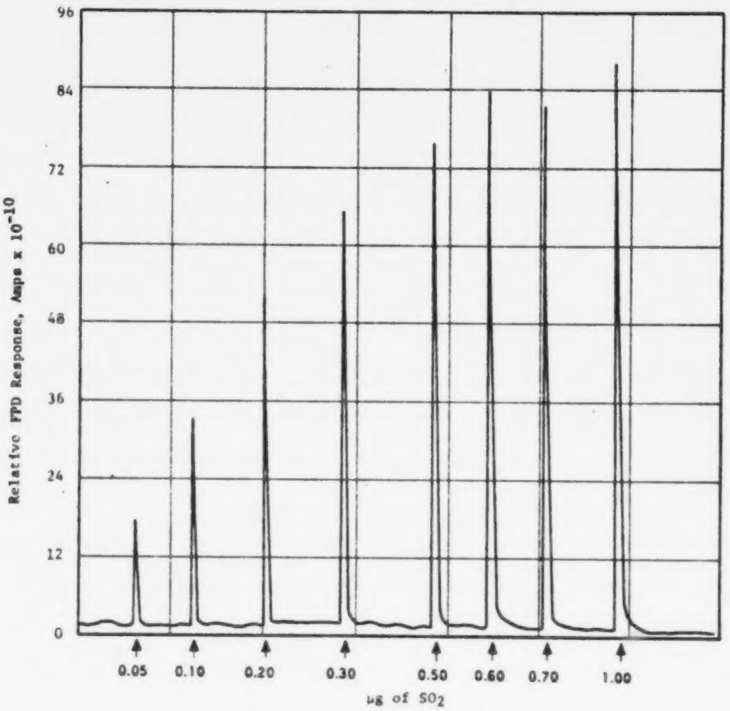


Figure 19. Quantitative FPD response to injected SO_2.

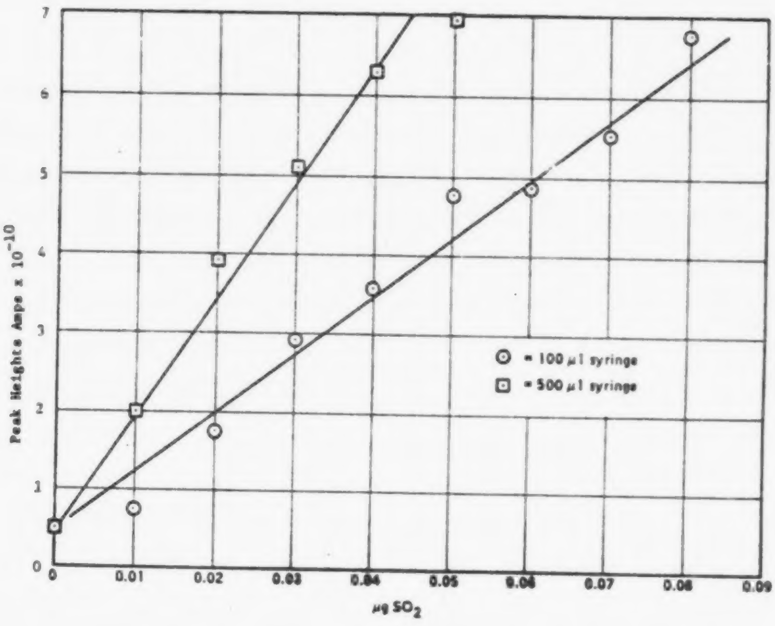


Figure 20. Quantitative response of FPD to SO_2.

syringe, causing some retention of SO_2 by glass surface. The response, however, was fairly linear from 0.01 μg up to about 0.6 μg, beyond which there was no further consistent increase in peak height. It was established on other electrometer settings that the saturation level always occurred at about 0.6 μg of SO_2 and did not depend upon the electronics of the instrument.

If the saturation level of the detector is 0.6 μg SO_2, the corresponding amount of H_2SO_4 is 0.9 μg. It is, therefore, not surprising that the large acid aerosol samples which gave the FPD recordings of Figure 17, and were estimated to contain 20 to 30 μg H_2SO_4 (by an independent pH measurement), did indeed saturate the detector.

These experiments, in which SO_2 was injected into the FPD, were crucial in the interpretation of the FPD recordings from aerosol samples. It was established that the peaks of Figure 17 were saturation artifacts, and, indeed, the H_2SO_4 aerosol samples which had been collected were too large. In subsequent runs, sampling procedures were modified to collect smaller samples and the resulting peaks resembled the unsaturated SO_2 peaks. The electrometer setting was at a range of 10 and attentuation at 32 during all remaining FPD experiments, which resulted in a full-scle recorder sensitivity of 10^{-10} amps.

DECOMPOSITION CHARACTERISTICS OF ADDUCTS (Unmodified Thomas Generator - 0.005 to 0.3 μm droplet)

The FPD analysis apparatus was used to analyze fixed aerosol samples from the Thomas aerosol generator by two major procedures. In the rising temperature procedure, the sample filter was inserted into the decomposition cell at room temperature. With carrier gas flowing through the cell to the FPD, the cell temperature was then slowly raised. The rising temperature procedure served only to determine the decomposition temperature of the various adducts and interferences. It was not considered to be an alternative to the proposed methodology, which consisted of adduct decomposition at fixed temperatures.

In the fixed temperature procedure, the sample was inserted into the decomposition cell which was preset at 120°C. After five minutes at 120°C the by-pass valve was switched and the evolved gases passed through the FPD with the aid of a helium carrier. The initial temperature of 120°C was chosen because DTA had previously shown that all of the adducts decomposed between 120 and 200°C. Thus, the 120°C temperature served only to volatilize residual unfixed H_2SO_4 aerosol, which, when detected by the FPD, gave an indication of the completeness of the fixing process for each candidate fixing reagent.

Once the 120°C step had been completed, the temperature of the decomposition cell was rapidly raised to 200°C, with the carrier gas again bypassing the cell. After five minutes at 200°C, the valve was switched to sweep gas evolved from the sample into the FPD. The temperature of 200°C was chosen as the second decomposition step, since DTA had shown that all of the adducts decompose below this temperature.

Rising Temperature Procedure (Unmodified Thomas Generator)

This procedure was used to determine the temperature at which any sulfur gas was first evolved from the sample. As the cell temperature increased, it was marked on the x-axis of a constant-feeding strip-chart recorder. The pen of the strip-chart recorder on the y-axis was connected to the FPD. The temperature at which the pen rose sharply from baseline was taken as the adduct decomposition temperature.

The results of this procedure strikingly revealed the effects of fixation on the collected aerosol. As shown in Table 7, the evolution of SO_2 in every case occurred at higher temperature with the fixed samples than with the unfixed H_2SO_4.

TABLE 7. TEMPERATURE OF INITIAL FPD RESPONSE FORM ADDUCTS (UNMODIFIED THOMAS GENERATOR)

	°C
H_2SO_4 Alone	90
H_2SO_4 + AAO	140
H_2SO_4 + DEHA	190
H_2SO_4 + DEA	190

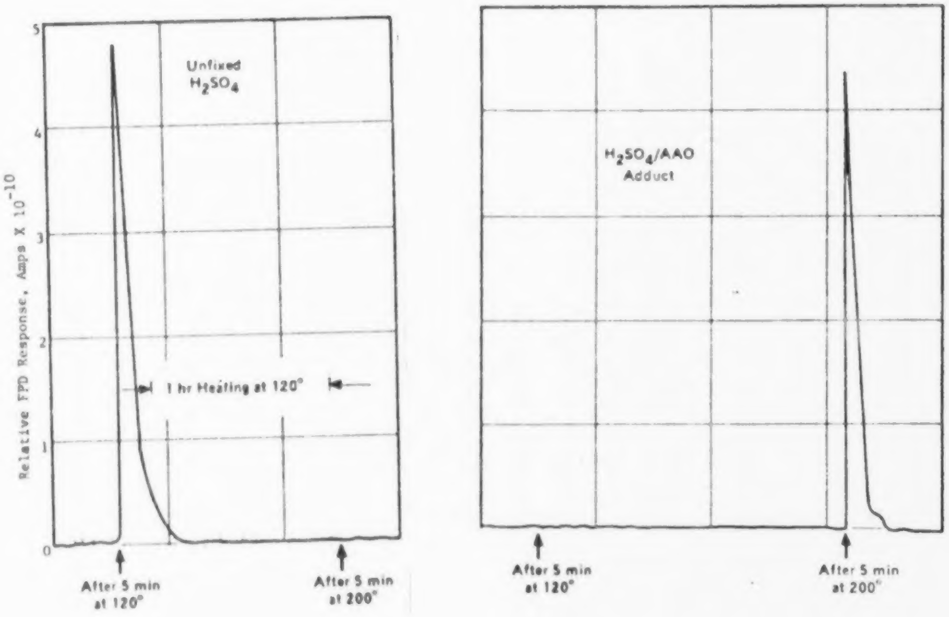
Multiple runs indicated that the decomposition temperatures were reproducible to within ± 10% of the values given in Table 7. This level of reproducibility was not an indirect effect of excess reagent on the filter, since the same results were obtained when the samples were thoroughly flushed with clean air prior to analysis. Of the three reagents, it appears that AAO forms the adduct which is easiest to thermally decompose.

Fixed Temperature Procedure (Unmodified Thomas Generator)

By holding the adduct in the sample cell for several minutes before sweeping it into the FPD, the evolved SO_2 is concentrated. This procedure is, therefore, more sensitive to small samples than the previous procedure. If care is taken to collect samples that are not too large, the peaks obtained when the gas is admitted into the FPD are sharp, and their height may be taken as a measure of the H_2SO_4 collected.

The results of the rising temperature procedure showing that the adducts decompose between 120 and 200°C were confirmed by the fixed temperature procedure. As can be seen in Figure 21, when the H_2SO_4 aerosol (Thomas generator) was not fixed, the FPD showed the presence of a sulfur gas at 120°C and additional heating at 200°C showed that all of the unfixed acid had been volatilized at 120°C. When H_2SO_4 aerosol (Thomas generator), however, was fixed by the simultaneous addition of AAO in the fixing chamber, the AAO adduct gave no FPD response at 120°C, but a pronounced response at 200°C. Thus, it was demonstrated that the acid aerosol was fixed completely and rapidly since no FPD response was detected at 120°C, even when only 15 seconds of reagent-acid contact was allowed after aerosol collection. Similar results were obtained for the DEHA and DEA adducts.

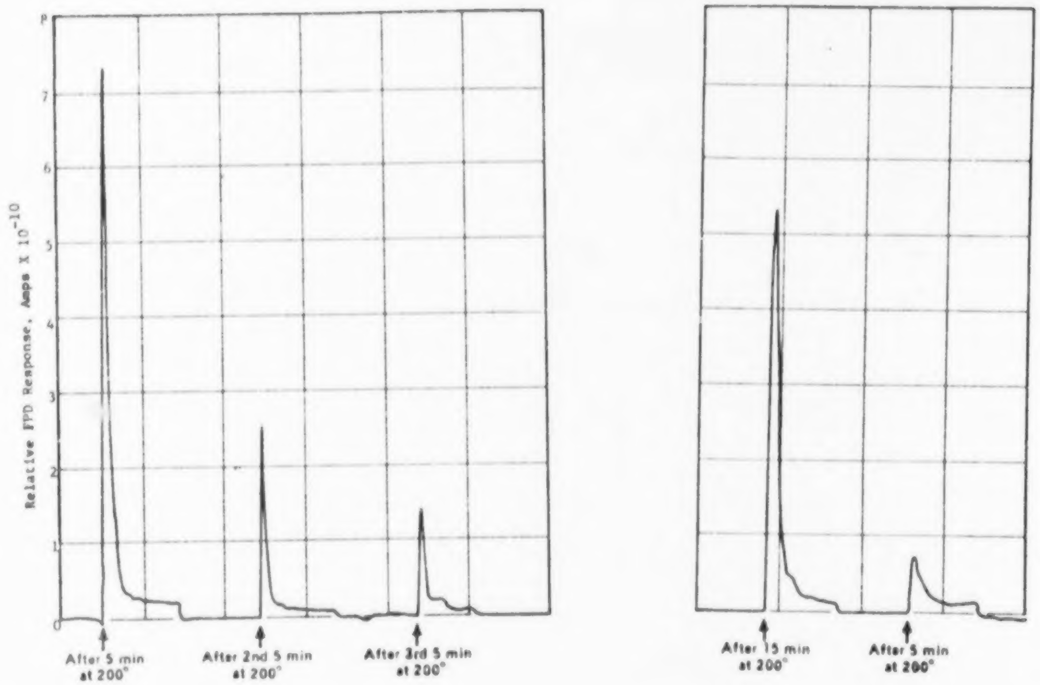
The rate of decomposition of the AAO-adduct at 200°C was also evaluated by the fixed temperature procedure. The procedure was to repeat the heating period, i.e., 200°C for 5 minutes, with the valve on bypass several times. As Figure 22 shows, the second peak was proportionately smaller when the first heating period was 15 minutes, than when it was 5 minutes. In other words, decomposition was more complete after 15 minutes (about 80%) than after 5 minutes (about 50%). When a particularly small (<20 ng)



A. Unfixed H_2SO_4

B. H_2SO_4/AAO adduct

Figure 21. Completeness of fixation by AAO (fixed temperature procedure).



A. Decomposition after Repeated 5 Minute Heating Periods.

B. Decomposition after Repeated 15 Minute Heating Periods.

Figure 22. Completeness of decomposition of AAO/H_2SO_4 adduct after 5 min (a) and 15 min (b).

sample was analyzed, decomposition seemed to be essentially complete after the first 5 minute period, as shown in Figure 23.

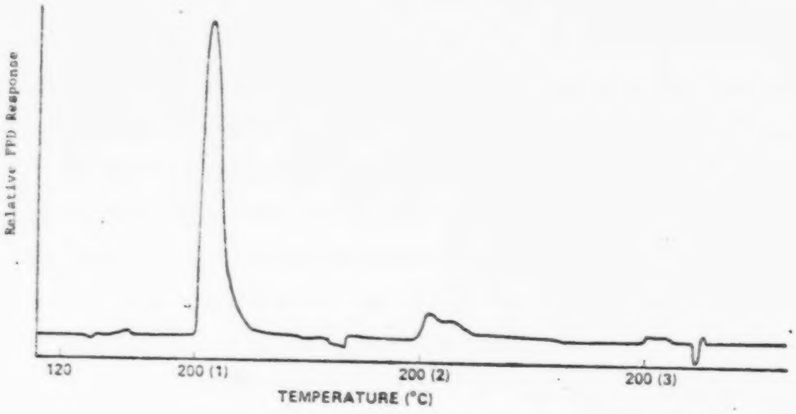


Figure 23. Typical FPD trace from AAO-treated sample.

From these experiments, it is evident that gas-phase fixation with these reagents occurs rapidly and completely, as indicated by a higher thermal stability of the fixed acid on the filter. The AAO-adduct is stable at 120°C, but is approximately 50% decomposed after 5 minutes of heating at 200°C. Finally, the FPD peak height demonstrates the amount of acid originally collected is on the order of 1 μg, which is anticipated for environmental samples.

Accuracy (Unmodified Thomas Generator)

The accuracy of an analytical method is defined as the degree to which the measurements obtained agree with the true value, as determined by an independent method of known accuracy. Alternatively, the accuracy can be determined by comparison of the measured values with a known standard concentration. Since there is no independent method of known accuracy for analysis of atmospheric H_2SO_4, the first approach cannot be strictly fulfilled. Moreover, the unpredictability of this type of aerosol generator (Thomas) makes it difficult to calculate the exact amount of acid deposited. Thus, neither of the above approaches allows for the absolute determination of accuracy when the Thomas generator is used as the H_2SO_4 aerosol source.

The Thomas generator was later modified to give more consistent aerosols and is discussed under the Modified Thomas Generator (page 91). The present discussion, however, will deal with the Thomas generator utilizing the original unmodified flame burner design.

One initial indication of accuracy which can be shown is that the measurement accurately reflects the difference between two samples of known size relationship to one another. The simplest manner in which to produce samples of a known size relation was to halve a sample filter, then halve it again, etc. Figure 24 shows the FPD trace obtained from each segment after 5 minutes at 200°C. The peak heights definitely showed the size order of the corresponding samples, although the magnitudes were not precisely uniform. This may have been due to nonuniform distribution of adduct on the filter, unsymmetrical cutting, or random sample loss during sampling.

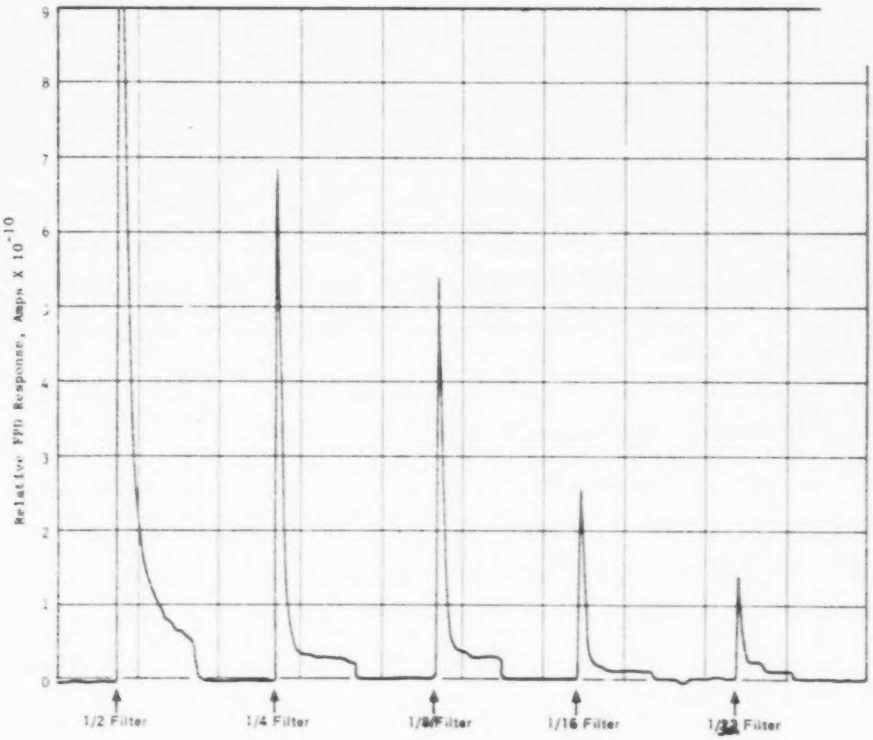


Figure 24. AAO-fixed filter portions after heating 5 min at 200°C.

In addition to the above tests, several different samples were generated by collecting different volumes from the aerosol generator (i.e., varying sampling time). Those which had filtered the largest volume of air also produced the largest peaks, as was expected. Figure 25 shows a plot of data obtained from these runs.

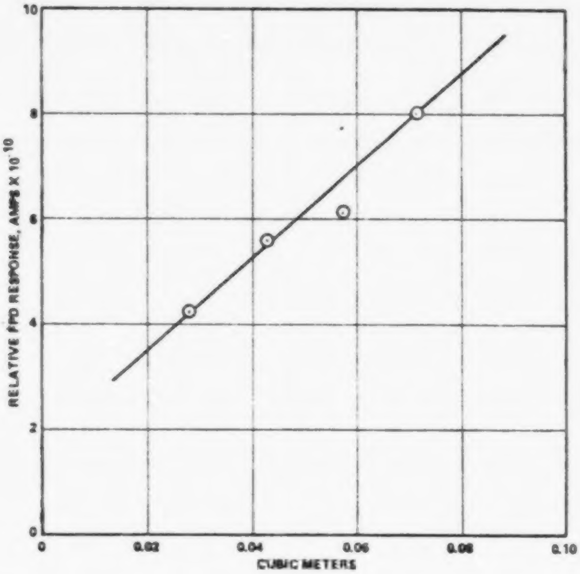


Figure 25. AAO-treated samples, different sampling volumes, 5 min. at 200°C.

It was concluded from these data that peak height was an indication of the amount of acid adduct in a sample. The only possible way to independently verify this measurement would be to prepare samples by a different method, with which the amount of acid placed on the filter would be known. Many researchers have employed micropipet deposition of dilute H_2SO_4-methanol or acetone solutions for this purpose. This approach was adopted later in the study, and is discussed on page 85.

Precision (Unmodified Thomas Generator)

Precision is the degree to which the values obtained by an analytical method are reproducible. Evaluation of precision placed stringent demands on the ability to generate known samples. Specifically, it was necessary to generate two or more samples containing the same amount of adduct with as little variation as possible. The similarity in peak heights from the identical samples was then a measure of precision. The Thomas aerosol generator used in these experiments was known to have poor reproducibility. The problem was approached by designing a sampling probe for the generator so that two samples could be collected simultaneously, and would, therefore, be identical. The data from a series of three runs are shown in Figure 26 and summarized in Table 8.

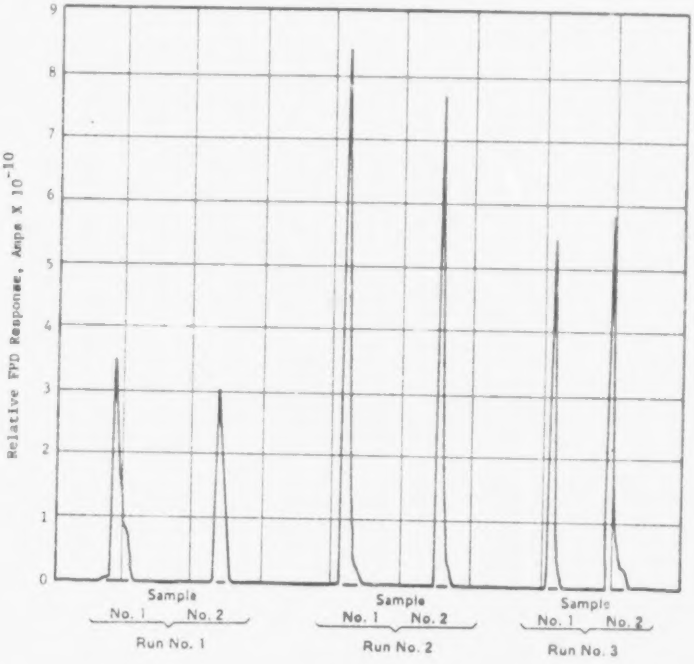


Figure 26. Pairs of AAO-fixed samples collected simultaneously.

TABLE 8. PEAK HEIGHTS OF SAMPLE PAIRS COLLECTED SIMULTANEOUSLY

	Peak Height		
Run	Sample #1	Sample #2	% Difference
1	3.4	3.1	10.0
2	8.3	7.7	7.2
3	5.4	5.8	6.9

For each pair of samples, the variation in peak height is no more than 10% It was concluded from this evidence that precision is no less than 90% and is probably greater.

Interference Studies (Unmodified Thomas Generator)

Ammonium Sulfate and Bisulfate --

Differential Thermal Analysis (DTA) of ammonium sulfate and bisulfate previously presented as Figure 13 indicated that these two salts are stable to at least 250°C and 230°C, respectively. The temperature at which these compounds release a sulfur-containing vapor in significant quantities is the subject of some dispute. Dubois, et al. (60) discussed the use of $(NH_4)_2SO_4$ as a standard for diffusion at 195°C. Maddalone, et al. (39) however, reported that a thermal gravimetric analysis (TGA) of $(NH_4)_2SO_4$ indicated no significant decomposition until 250°C, in agreement with the present results. Erdey, et al. (61) have reported the following reactions:

$$(NH_4)_2SO_4 \xrightarrow{250\text{-}350°C} NH_4HSO_4 + NH_3$$

$$NH_4HSO_4 \xrightarrow{250\text{-}350°C} NH_3 + H_2SO_4$$

Experiments with the FPD indicated that no volatile sulfur species were released by either of these salts until at least 240°C, and there was some ambiguity when a signal was recorded at this higher temperature, due to background sulfur in the system. Ammonium sulfate and bisulfate, finely ground from a reagent bottle, gave no signal at 200°C with either of the procedures described in the preceding section. When ammonia was passed through a filter on which the acid aerosol had been collected unfixed, as is normally the case in environmental sampling, no signal was detected at 200°C. Interference from this source was apparently not present.

Sulfur Gases--

Since the FPD responds to sulfur in any form, it was recognized that the ambient sulfur gases, SO_2, H_2S and COS, may interfere by reacting with the gaseous reagent. They may then be collected on the filter as a sulfur-gas reagent complex. These sulfur gas-reagent complexes would interfere with H_2SO_4 adduct measurement, if their thermal stability was similar to that of the adduct.

To test this possibility, each of these gases was mixed with reagent vapor in a glass "Y" and drawn through a filter for several minutes. The filter was analyzed by the rising temperature procedure in order to determine both the presence of a volatile sulfur species and the temperature at which it was produced.

As shown in Table 9, of the three gases, only SO_2 was significantly collected, and in every case, the SO_2-reagent complex had a very low thermal stability compared to the H_2SO_4-adduct. This was independently verified by mass spectral evidence. Figure 27 compares the FPD recordings obtained using the rising temperature procedure for unfixed acid, AAO-fixed acid, AAO-SO_2 complex, and $(NH_4)_2SO_4$.

TABLE 9. TEMPERATURE (°C) OF FIRST FPD RESPONSE FROM SULFUR GAS-REAGENT COMPLEXES

	SO_2	H_2S	COS
DEA	25	60*	-
DEHA	25	-	-
AAO	30	-	-

*Very little absorbed

First, it appears that a fairly high concentration of SO_2 (>25 ppm) must be present before a significant amount is collected. Sulfur dioxide was being produced by the aerosol generator in low concentration (5 ppm by Dräger tubes), but none was ever detected at the 120°C step during routine runs. Secondly, even if sufficient concentration is present, the collected complex can be rapidly and selectively removed from the sample at 100°C, prior to H_2SO_4-adduct analysis.

The chemical nature of these compounds is uncertain. Grundnes, et al. (62) have examined the formation of charge-transfer complexes in the gas phase reaction of SO_2 with amines. Studies of the analogous reaction

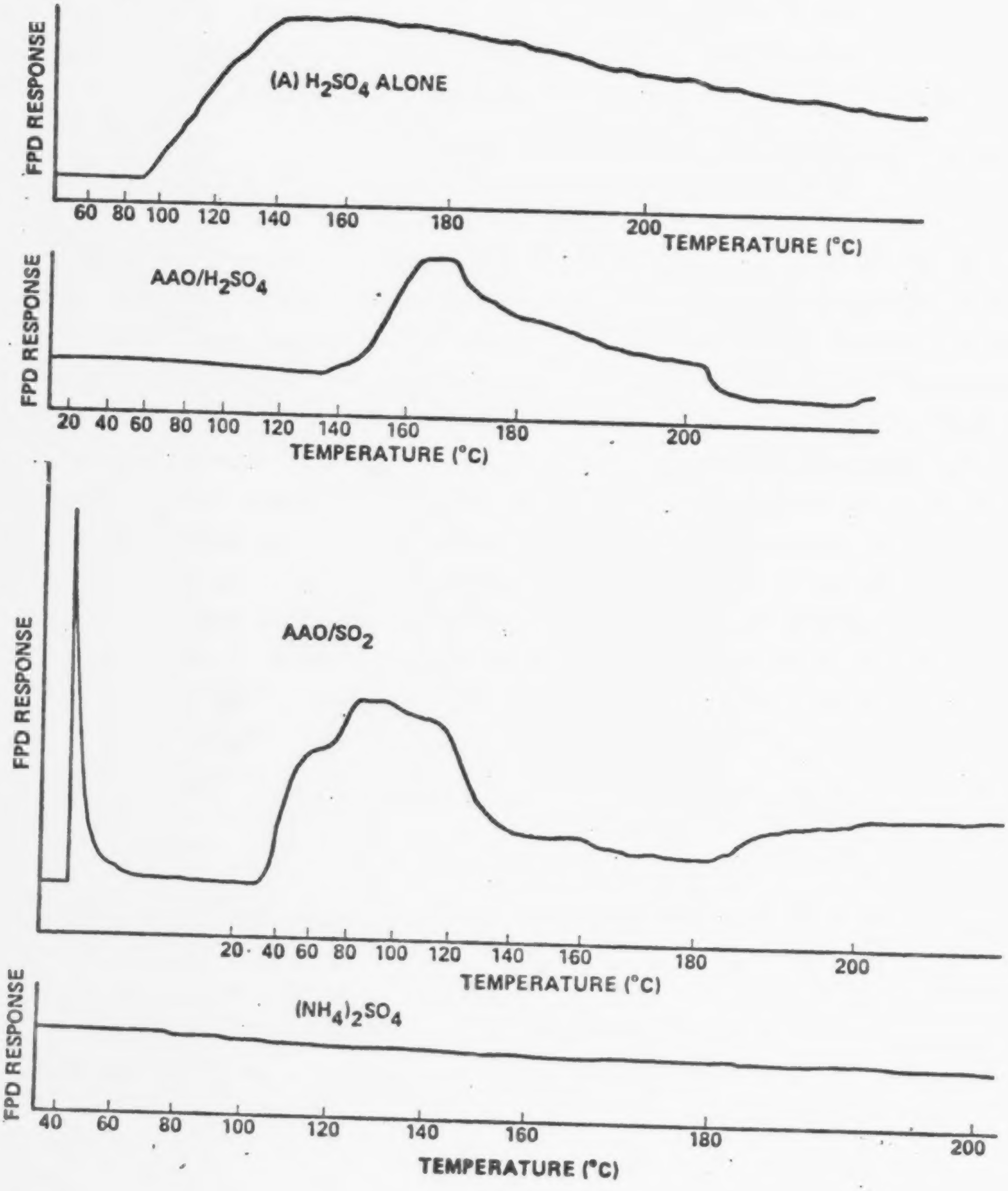


Figure 27. Continuous heating procedure - FPD recordings from H_2SO_4 samples.

between SO_2 and NH_3 have found mostly sulfite and bisulfite salts (63,64). It may be possible, however, for the collected SO_2 to be oxidized to SO_4^{-2}, if catalytic conditions are present (64). For this reason, it might be desirable to heat the filter to approximately 60°C during collection, so that SO_2-reagent complexes are immediately decomposed and removed.

Summary (Unmodified Thomas Generator, 0.005 to 0.3 μm)

Studies using the Thomas aerosol generator showed that highly volatile amines and amine-derivative reagents could be used to fix sulfuric acid aerosol during the collection process. Furthermore, it was found that the fixing reaction proceeded at a sufficiently rapid rate for quantitative fixing and was complete during reactor residence time. A correlation was established between the sulfur gases evolved during the adduct decomposition and the amount of sulfuric acid aerosol stream sampled. In addition, it was found that the amount of sulfur gases evolved during adduct thermal decomposition of identical samples was reproducible. The ammonium sulfate salts, which are thought to be the most problematic interfering species in the analysis of ambient H_2SO_4 were found to have decomposition temperatures that were measurably distinct from the sulfuric acid adducts. Thus, it was demonstrated that H_2SO_4 adducts made from aerosols in the 0.005 to 0.3 μm size range, could be differentiated from ammonium sulfate salts.

DECOMPOSITION CHARACTERISTICS OF ADDUCTS (Baird Generator, 1 to 3 μm Droplets

The Baird aerosol generator, described on page 43 of this report, was originally selected for this study because of a need for aerosol particles in the 1 to 3 μm size range. It was, however, also anticipated that the generator, because of the closed system design, would give highly reproducible aerosols. The FPD analysis apparatus was used to analyze fixed aerosol samples from the Baird Generator by procedures identical to those used with the Thomas generator.

Adduct Decomposition (Baird Generator)

Initially, the adducts formed using the Baird generator were decomposed using the rising temperature procedure in order to verify decomposition temperatures. The results were surprising in that the three adducts previously investigated using the Thomas generator now had average decomposition temperatures that were different. The results are given in Table 10, along with a comparison of results obtained from the Thomas generator and from depositing H_2SO_4 on Mitex filters using the micropipet technique discussed on page 45.

TABLE 10. INITIAL H_2SO_4 DECOMPOSITION TEMPERATURE BY H_2SO_4 GENERATION METHOD.

H_2SO_4 Adduct	Thomas Generator °C	Baird Generator °C	Pipet °C
AAO	140	185	195
DEA	190	200	200
DEHA	190	170	185

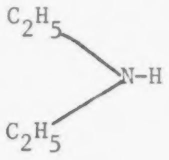
As can be seen from the table, the average decomposition temperature of the AAO and DEA adducts shifted upward while the third (DEHA) shifted downward. Of the three adducts, only that of AAO showed a substantial change compared to the previously determined individual decomposition temperature reproducibility of ± 10%. Experiments were also performed, as shown in Table 11, using a pipet to deposit the various reagents directly onto Mitex filters. It was found that the AAO adduct decomposed at 195°C, the DEA at 200°C, and the DEHA at 185°C. Again, only the AAO adduct showed a significant difference in decomposition temperature as compared to those formed using the Thomas generator.

The results of the experiments described above made it necessary to re-evaluate some of the previous work with amine-derivative reagents. A comparison between samples applied with a pipet and samples applied with the aerosol generators was again made, using the three candidate reagents: acetaldoxime (AAO), diethylamine (DEA) and the new reagent, n-methylformamide (NMF). The average initial decomposition temperatures of the AAO and NMF adducts were found to be affected by the mode of aerosol deposition as shown in Table 11.

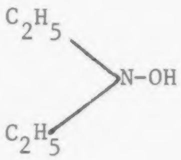
TABLE 11. INITIAL H_2SO_4 ADDUCT DECOMPOSITION TEMPERATURES BY H_2SO_4 GENERATION METHOD

Sample Generation	AAO °C	DEA °C	NMF °C
Pipet	195	200	193
Baird Aerosol	180	200	185
Thomas Aerosol	140	190	120

Examination of the above data indicated several possible reasons for the observed decomposition temperature fluctuations. One explanation was that the various aerosol generation methods which were selected to give droplets of different size ranges also resulted in particles with a large difference in free surface energy (due to significant differences in particle size). The difference in free surface energy between particles of greatly varying size resulted in a corresponding change in the decomposition temperature. However, the data suggest that the mode of aerosol generation was a significant factor only when the fixing reagent contained unsaturated bonds. For example the DEA and DEHA fixing reagents,

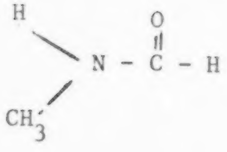


DEA

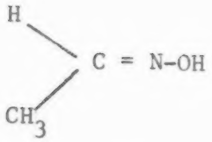


DEHA

have no unsaturated bonds and the corresponding H_2SO_4 adducts gave average decomposition temperatures of 195°C and 180°C, respectively, regardless of the H_2SO_4 generation method. The NMF and AAO fixing reagents, however,



NMF



AAO

which have unsaturated bonds, consistently resulted in decomposition temperatures which reflected the method of aerosol generation. The decomposition temperature for the NMF and the AAO adducts of H_2SO_4 using the Baird aerosol generator averaged 185°C and 180°C, respectively, while use of the Thomas aerosol generator results in the NMF adduct having an average decomposition temperature of 120°C and the AAO adduct having an average decomposition temperature of 140°C. Thus, it appeared that the chemical nature of the fixing reagent, in conjunction with the aerosol generation method, affects the decomposition temperature of specific H_2SO_4 adducts. This may be due in part to the fact that the collection temperature of the Thomas generator was approximately 60°C, while the Baird generator aerosol was collected at approximately 30°C. The higher temperature of the Thomas generator was due to the use of a flame during aerosol formation.

Ammonium Sulfate Interferences

The questions associated with the decomposition of the various adducts led to a re-investigation of the major anticipated interferent, $(NH_4)_2SO_4$. Several sets of experiments were performed to accumulate data which might point to the reason for the decomposition temperature deviations. A series of 0.01N $(NH_4)_2SO_4$ samples from the same solution were deposited in different volumetric amounts by micropipet on Mitex filters. These tests were performed to determine if different quantitative amounts of aerosol could cause the temperature fluctuations. Results of these experiments are given in Table 12. As can be seen from the table, the initial FPD response from the decomposition of identical $(NH_4)_2SO_4$ samples occurred over a range of 170°C to 195°C. Since the samples were prepared and analyzed under identical conditions, it would appear that the inconsistency is not related to quantitative differences in the amount of $(NH_4)_2SO_4$ deposited.

TABLE 12. SUMMARY OF $(NH_4)_2SO_4$ DECOMPOSITION TEMPERATURES FOR VARIOUS SAMPLE SIZES.

Sample Size (μl)	Initial FPD Response (°C)
5	190
5	190
7	190
7	195
7	175
10	170
10	185
10	190
15	175
15	170
15	180

The Baird generator was used to deposit $(NH_4)_2SO_4$ aerosols made from 0.01N and 0.001N $(NH_4)_2SO_4$ solutions. It was assumed that since less $(NH_4)_2SO_4$ per droplet would be present, this would result in a smaller particle when dry. The aerosol was prepared by simply dissolving $(NH_4)_2SO_4$ into deionized water to give a 0.01N and a 0.001N solution and aspirating these solutions through the Baird generator instead of sulfuric acid solutions. The 0.01N solution was also deposited on a filter using a pipet and subjected to the same temperature programming sequence. In addition, $(NH_4)_2SO_4$ was formed using H_2SO_4 aerosol obtained from the Thomas generator. The $(NH_4)_2SO_4$ in this case was formed by passing anhydrous NH_3 through the fixing chamber as the H_2SO_4 aerosol was generated, or alternatively, by first collecting the H_2SO_4 aerosol, waiting ten minutes, and then passing NH_3 through the filter. The results of these experiments are given in Table 13. It should be pointed out that the results given in the table are average values obtained from a minimum of 5 individual runs for a specific experiment.

TABLE 13. INITIAL RESPONSE OF FPD FOR $(NH_4)_2SO_4$ BY DEPOSITION METHOD.

Average Initial FPD Response (°C)	Deposition Method
240	$(NH_4)_2SO_4$ from reagent bottle
183	Pipet, 0.01N solution
175	Aerosol, Baird, 0.01N solution
165	Aerosol, Baird, 0.001N solution
158*	Aerosol, Thomas, 0.01N solution
220**	Aerosol, Thomas, 0.01N solution

*$(NH_4)_2SO_4$ prepared by fixing H_2SO_4 aerosol with NH_3 during sample collection.

**$(NH_4)_2SO_4$ prepared by fixing H_2SO_4 aerosol with NH_3 after sample collection.

As can be seen from Table 13, $(NH_4)_2SO_4$ taken from a reagent bottle and ground to a fine powder gave an average initial decomposition temperature of 240°C.

When the Baird aerosol generator was used to deposit samples from a solution of 0.01N $(NH_4)_2SO_4$, an average value of 175°C was found to be the initial temperature at which the aerosol decomposes. However, when the identical solution was deposited by pipet and subjected to the same analysis procedures, an average decomposition temperature of 183°C was obtained. When the Baird generator was used to deposit the 0.001N $(NH_4)_2SO_4$ solution, the initial response temperature dropped to an average of 165°C. Use of the Thomas generator and exposure of the generated H_2SO_4 aerosol to NH_3 during sample collection resulted in a further drop of the $(NH_4)_2SO_4$ initial decomposition temperature to an average of 158°C. When the H_2SO_4 aerosol is first collected, however, and then exposed to NH_3, the initial $(NH_4)_2SO_4$ decomposition temperature rises to an average of 200°C. It was thought that the lack of agreement in results obtained using the Thomas generator, with alternate $(NH_4)_2SO_4$ formation procedures, was due to H_2SO_4 aerosol droplet growth on the collection surface prior to the addition of NH_3.

An examination of the various H_2SO_4 generation methods suggested that each would result in particles of different size ranges being deposited. Thus, it appeared that a particle size effect might be inducing a corresponding change in decomposition temperature of the $(NH_4)_2SO_4$. This possibility was discussed with two independent scientists involved in sulfuric acid aerosol research, Dr. Herbert Miller of Southern Research Institute (65) and Dr. Willard Richards of Rockwell International (66). The consensus was that the particle size deviations anticipated from the various generators was most probably the reason for the decomposition differences. It is interesting to note that Dr. Miller, while using the Thomas generator in an analogous manner to prepare $(NH_4)_2SO_4$ aerosol (collecting H_2SO_4 aerosol on the filter, then passing NH_3 through it) also found no decomposition at 220°C. Dr. Richards, on the other hand, routinely used the Baird generator to make aerosols and found that $(NH_4)_2SO_4$ begins to decompose at approximately 160°C.

Several experiments were also performed to see if altering the flow or temperature programming rate of the volatilization/decomposition chamber might induce a change in the initial decomposition temperature of $(NH_4)_2SO_4$. It was thought that the difficulty in reproducing initial decomposition temperatures for $(NH_4)_2SO_4$ might be due to subtle changes in these conditions. Moderate changes, however, in the rate of heating ($\pm$ 10°C/min) or carrier gas flow ($\pm$ 25 cc/min) did not noticeably change the initial response temperatures of $(NH_4)_2SO_4$.

Thus, it was concluded that the particle size of aerosols does influence the decomposition temperatures of the various adducts to a large degree. This is particularly significant since the distribution of sulfuric acid aerosols in the environment is thought to cover a large size range which would indicate that the corresponding adduct decomposition would also vary widely.

Aerosol Stoichiometry (Baird Generator)

Experiments were performed to obtain information regarding the reproducibility of the Baird generator and the quantities of SO_2 evolved from the AAO adducts. Four trials were made which were identical with respect to aerosol generating parameters and the volume of H_2SO_4 solution passed through the Baird nebulizer. The filters were heated at 200°C for 30 minutes and the evolved gases determined by the West-Gaeke method. The results of these expeirments are given in Table 14.

TABLE 14. RECOVERY OF SO_2 FROM AAO/H_2SO_4 ADDUCT (DRY AIR)

Run No.	Aspiration Volume (ml)	Volume Consumed (ml)	μg H_2SO_4
1	25	2	8.0
2	25	2	7.5
3	25	2	7.0
4	25	2	8.5

As can be seen from Table 14, the amount of H_2SO_4 collected during each run was fairly reproducible based upon the amount of SO_2 evolved during the thermal decomposition process. Thus, it appears that the Baird generator is fairly reproducible, as is the evolution of SO_2 from an identical quantity of the AAO adduct. However, based upon an aspiration volume consumption of 2 ml (0.001N H_2SO_4 solution), 98 μg of H_2SO_4 should theoretically have been collected. Instead, an average of 7.7 μg were collected, resulting in an apparent collection efficiency of approximately 7.9%.

The fact that 75 ml of acid solution passed through the Baird nebulizer in the first experiment and 25 ml in the second experiment both resulted in 2 ml of solution being consumed could not be explained. It was thought that the large amount of solution lost during each run might be due to volatilization of water, since dry compressed air was used to operate the Baird nebulizer. Therefore, the above experiment was repeated using humidified air. The air was humidified by bubbling through a column of water which was 2.5 cm x 30.5 cm. The results of this experiment are given in Table 15.

As can be seen from Table 15, using humidified air decreased the volume of acid solution consumed to 1.8 ml, while the amount of adduct collected remained proportional to the volume of acid passed through the nebulizer. In fact, the 13.8 μg of acid collected when 50 ml of acid was

TABLE 15. RECOVERY OF SO_2 FROM AAO/H_2SO_4 ADDUCT (HUMIDIFIED AIR)

Run No.	Aspiration Volume (ml)	Volume Consumed (ml)	µg H_2SO_4
1	50	1.8	14.5
2	50	1.8	12.6
3	50	1.8	14.5
4	50	1.8	13.5

passed through the nebulizer is on the order of twice the 7.8 µg collected when 25 ml of acid was used. In addition, the 75 ml passed through the nebulizer in the first experiment resulted in 21 µg being recovered, which is approximately three times the 7.8 µg collected when 25 ml were passed through the nebulizer.

The aspiration rate of acid solution through the nebulizer of the Baird generator was maintained at 1.7 ml/min throughout the above experiments. The delivery of 1.7 ml/min required a continuous air flow of 34 l/min across the nebulizer orifice. Therefore, 25 mls of acid solution aspirated through the nebulizer used 500 l of air, while 50 ml of acid solution used 1000 l of air and 75 ml of acid solution used 1500 l of air. Since the entire aerosol stream from the Baird generator was sampled in the above experiments, it follows, as shown in Figure 28, that AAO can be used to fix H_2SO_4 aerosol in a moving gas stream to form an adduct which when decomposed gives off an amount of SO_2 that is related to the volume of aerosol stream sampled. However, the question of exact stoichiometric relationship between the evolved SO_2 and the original H_2SO_4 aerosol stream can only be determined by the decomposition of a precisely known amount of H_2SO_4 adduct.

Summary (Baird Generator, 1 to 3 µm)

It was found that the decomposition temperature of the various H_2SO_4 adducts was, to some extent influenced by the particle size of the H_2SO_4 droplets from which the adduct was formed. This questions of the significance of environmental particle size on actual adduct decomposition

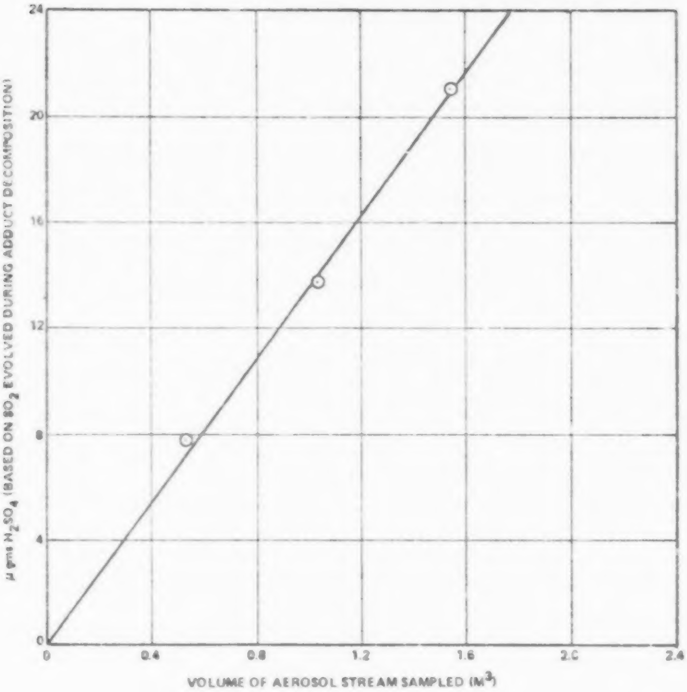


Figure 28. Relationship of aerosol sample volume and evolved SO_2 from AAO adduct decomposition.

characteristics should be investigated using an aerosol source which more closely duplicates actual environmental conditions. It appears that the larger particles in a real sampling situation would most probably have reacted with NH_3 to form $(NH_4)_2SO_4$, while the smaller particles would tend toward H_2SO_4 aerosol. This, of course, would ultimately depend upon prevailing environmental conditions, i.e., humidity, ambient ammonia content, etc. It was felt that the sampling of any pure aerosol generator stream tends to subject the analytical methodology to equilibrium characteristics which are not necessarily representative of actual environmental samples.

Attempts to correlate pH and sulfate level differences between the original acid and that returned to the trap were unsuccesful due to the concentration of the acid in the nebulizer trap being too great to accurately measure the small amount of acid lost during aerosol generation. It was, therefore, necessary to find an alternative method for depositing known amounts of H_2SO_4.

CHARACTERISTICS OF ADDUCT DECOMPOSITION GASES

The success of the proposed research approach ultimately depends upon whether a reproducible stoichiometric relationship exists between the sulfur gases evolved during adduct decomposition and the H_2SO_4 originally present in the sample stream. It was originally hypothesized that the gases evolved during adduct decomposition should consist primarily of SO_2. This was a desirable characteristic since SO_2 is relatively easy to quantitate and is a fairly stable species. It would serve little purpose to generate a highly reactive species, such as SO_3, which would subsequently partially react and be lost prior to quantitation. Thus, for the above reasons, SO_2 was selected as the initial gaseous species by which the stoichiometry of the proposed method would be evaluated. The West-Gaeke technique, because of its reported selectivity and sensitivity for SO_2, was chosen as the detection method for these tests. The FPD is not specific for SO_2 and would offer little toward defining the exact stoichiometric relationship of evolved SO_2, should other sulfur gases be present.

Specificity of West-Gaeke Technique for SO_2

The specificity of the West-Gaeke technique for SO_2 was examined by preparing various samples using the Baird aerosol generator and collection techniques previously described on page 50. The samples examined consisted of the following:

1. Clean, unused filter (all filters Mitex LS, 5 μm).
2. Filter through which 2 ml of deionized water and 515.4 liters of clean air had been sampled. (2 ml based on 75 ml passed through Baird atomizer and 73 collected in trap.)
3. Same as (2) above, but "fixed" with acetaldoxime vapor.
4. Filter through which 2 ml of 0.001N H_2SO_4 and 515.4 l of clean air had been sampled. (2 ml based on 75 ml passed through Baird atomizer and 73 collected in trap.)
5. Same as (4) above, but fixed with AAO vapor.

Each of the above samples was decomposed separately in the decomposition chamber for a period of one-half hour at a temperature of 200°C. The gaseous products were continuously bubbled through 10 ml of sodium tetrachloromercurate and subjected to the West-Gaeke analysis for SO_2. The results of these analyses are shown in Table 16.

TABLE 16. SPECIFICITY OF WEST-GAEKE TECHNIQUE FOR SO_2.

No.	Sample	% Absorbance	μg SO_2	μgm H_2SO_4
1	Clean filter	1	0	0
2	Water + air	1	0	0
3	Water + air + AAO vapor	1	0	0
4	0.001N H_2SO_4 + air	1	0	0
5	0.001N H_2SO_4 + air + AAO vapor	28	14	21
6	TCM blank	0	0	0

As can be seen from Table 16, the results indicate that the West-Gaeke technique is sensitive only to SO_2 and does not detect H_2SO_4 or the AAO-fixing reagent.

Pipet Adduct Characteristics

AAO Adducts --

The results of the experiments previously described using the Baird sulfuric acid generator indicated that it was probable that the apparent low decomposition yields with the AAO adduct were the results of complex decomposition products or the inability to quantitate the aerosol generator, rather than the actual collection or fixation efficiency. This was substantiated by the results obtained using the Thomas generator and the FPD method of detection which clearly showed no residual acid remained on the collection filter when similarly fixed. To further test the above hypothesis, however, and determine the actual stoichiometric SO_2 evolution relationship of several adducts based upon the amount of acid deposited, a set of experiments was devised in which a known amount of acid was applied directly to the filter media by micropipet.

Several Mitex Teflon filters were loaded with 600 μg of H_2SO_4 by pipet and the amount of H_2SO_4 determined turbidimetrically. The purpose of these experiments was to determine if 600 μg of acid could be reproducibly deposited on the filters and analyzed turbidmetrically. Several types of filters were used to obtain background information of the different media. As can be seen from Table 17, all filters except the glass fiber filter demonstrated 100% recovery. It is interesting to note that the high $SO_4^=$ reading on the glass fiber medium corresponds to Dubois' (37) findings that glass fibers contain residual sulfates.

TABLE 17. TURBIDIMETRIC ANALYSIS OF RAW H_2SO_4

Run No.	Filter	μgm H_2SO_4 Applied	μgm H_2SO_4 Measured
1	Whatman #40	600	600
2	Blank Whatman #40	0	0
3	Class Fibre	600	750
4	Fluoropore	600	600
5	Mitex	600	600

Once it was established that 600 μgm could be deposited and analyzed reproducibly, several filters were loaded with 600 μgm of H_2SO_4 and fixed with 25 μl of AAO. The samples were dried at 60°C for one hour, and the sulfate content determined turbidimetrically. These tests were designed to show that sulfur is not lost during the fixation process. As can be seen from Table 18, the results indicate that reproducibility of the fixation/drying process was on the order of ± 10%.

TABLE 18. SULFURIC ACID/AAO ADDUCT ANALYSIS
(LS FILTER - TURBIDIMETRIC ANALYSIS)

Run No.	μg H_2SO_4 Applied	μl AAO Applied	μgm H_2SO_4 measured
1	600	25	650
2	600	25	552
3	600	25	552

Four filters were then loaded with 600 μgm of H_2SO_4 and 25 μl of AAO and allowed to dry at 60°C for one hour. The adduct was decomposed at 200°C for 30 minutes. The evolved gases were determined by the West-Gaeke method and by bubbling the evolved gases into 10 ml of 0.6N H_2O_2 which was analyzed for total sulfate turbidimetrically. The H_2O_2 solution was used to oxidize SO_2 in the effluent to $SO_4^=$ (67). As can be seen from Table 19, it appears that additional sulfur species are generated during the decomposition process with approximately 30% of the sulfur present in the sample being accounted for as SO_2.

TABLE 19. DECOMPOSITION EFFICIENCY OF AAO ADDUCT

Method	Reagent	μgm H_2SO_4 Applied	μgm H_2SO_4 measured
West-Gaeke	AAO	600	199
West-Gaeke	AAO	600	184
H_2O_2	AAO	600	235
H_2O_2	AAO	600	296

Subsequent turbidimetric analysis of the filter material from the above samples for sulfur indicated that all sulfur species were totally removed during the decomposition process. Analysis of the connecting tubing between the decomposition chamber and the collection solutions showed the presence of $SO_4^=$. These analyses, however, accounted for only an additional 30% of the sulfur anticipated from the decomposition of the adduct. The odor of H_2S gas was noted in several cases during adduct decomposition, but no effort was made to quantitate for other sulfur species. Thus, even though the West-Gaeke analyses from both the micropipeted samples and those prepared using the Baird aerosol generator have consistently showed a reproducible relationship between sample size and SO_2 evolution from the decomposed AAO adducts, the fact that several sulfur species are present makes consistent accurate quantitation of the adduct by this method subject to possible perturbations. However, the stoichiometric relationship between the SO_2 evolved during adduct decomposition and the original acid aerosol was reproducibly one mole of SO_2 to three moles of H_2SO_4 when both sampling and analysis were accomplished under controlled laboratory conditions. It would be more desirable to have an H_2SO_4 adduct that decomposes to give a 100% stoichiometric return of SO_2 based upon the amount of acid originally present in the sample.

DEA and DEHA Adducts --

It appeared that the reason for the failure of the adduct of AAO to return 100% of the sulfur decompositon produce as SO_2 is due to the formation of several species during the decomposition process. Because the presence of several sulfur containing species in the adduct decomposition gas stream makes it more subject to quantitation errors, it was decided to test several other candidate H_2SO_4 adducts for less complicated decomposition mechanisms. It was felt, based upon structural differences, that diethylamine was the best candidate for investigation.

The West-Gaeke technique was used to determine the stoichiometric relationship of the SO_2 evolved during the decomposition of the DEA adduct. All samples were prepared by depositing 600 μg of H_2SO_4 onto Mitex filters by micropipet. Immediately after the H_2SO_4 was deposited, an excess of DEA was added (25 μl) and the adduct allowed to dry at 100°C. When dry, the filters were placed in the sample chamber and then heated to ≈ 200°C for one hour, while the evolved gases were purged by helium into the TCM solution (West-Gaeke). Aliquots of the TCM were then taken and developed in the usual manner for comparison with SO_2 standards. The results of these tests are given in Table 20.

TABLE 20. DECOMPOSITION OF DEA ADDUCT (SO_2 ANALYSIS)

Run No.	μg H_2SO_4 deposited	μg SO_2		μgm Equivalent H_2SO_4 Found
1	600	341		522
2	600	387		592
3	600	398		610
4	600	350		540
5	600	406		621
6	600	429		656
			Average	590

Thus, it appears that virtually all of the H_2SO_4 deposited on the filters can be accounted for, based upon the SO_2 evolved during DEA adduct decomposition. This is a desirable property since it simplifies analytical methodology.

Several tests were also made with diethylhydroxylamine. The adduct was heated for one hour and yielded an average of 318 μg of H_2SO_4. It appears at this point that diethylamine offers the most promising recovery of adduct decomposition products with the least problems.

In summary, the DEA adduct of sulfuric acid returns the best stoichiometric ratio of SO_2 when thermally decomposed of the three adducts examined.

Adduct Stability

As originally conceived, a desirable aspect of the proposed methodology was the prediction that the H_2SO_4 adducts would be less likely to react during the collection process than the original acid aerosol. It was also predicted that drying of the adducts would have a tendency to suppress side reactions on collection surfaces. The lower reactivity of the adducts should, in effect, minimize the significance of negative interferences due to the loss of H_2SO_4. Thus, any feasibility assessment of the proposed methodology must necessarily incorporate an investigation to determine if the adducts are less subject than H_2SO_4 aerosol to undergoing reaction during the collection process. Therefore, experiments were performed to compare the reactivity of various adducts (both wet and dry) with NH_3 and the reactivity of H_2SO_4 aerosol with NH_3. Ammonia was selected as the test species because of its reactivity with H_2SO_4 and because it is easily exposed in a homogeneous manner to both the adducts and the acid aerosol on the collection surface.

The reactivity of sulfuric acid aerosol with ammonia was determined by passing a gaseous mixture of 250 ppm ammonia through the reaction chamber of the sample collection device concurrently with H_2SO_4 aerosol from the Baird generator. The amount of NH_3 reacted with the sulfuric acid aerosol was then measured with an ammonia specific ion electrode. Basically, this procedure involved removing each sample from the collection device and placing it in 100 ml of deionized water. One ml of 10 molar NaOH was then added to the solution to generate NH_3. The ammonia concentration as measured by the specific ion electrode, served as an indication of the amount of ammonia which had reacted with the H_2SO_4 aerosol.

Blank samples were prepared by exposing various fixing reagents to H_2SO_4 aerosol from the Baird generator in a manner analogous to ammonia above. The blank samples were then measured with the ammonia specific ion electrode. These tests served to show that the adducts themselves gave very little response on the NH_3 electrode. Identical adducts were then prepared using the Baird generator and subsequently exposed to a mixture of 250 ppm ammonia for exactly the same length of time as the original H_2SO_4 aerosol.

In the case of experiments studying the reactivity of wet aerosols, the adducts were exposed immediately after being formed to a dynamic ammonia environment of 250 ppm. In the case of experiments studying dried adducts, the freshly formed adducts were removed from the sampler, placed in a closed Petri dish and dried for approximately one day at 85°C. The dried samples were then returned to the sampler and exposed to a dynamic ammonia environment of 250 ppm for the same period of time as the original undried samples.

Analysis of both wet and dry samples involved removing the filter from the collection device and placing them in 100 ml of deionized water. One ml of 10 molar sodium hydroxide was then added to the solution to generate NH_3 which was detected by the ammonia specific ion electrode. The ammonia concentration, reactor flow rate, aerosol generation rate, and ammonia exposure time were identical in all experiments.

Ammonium sulfate was formed by passing a gaseous mixture of 250 ppm ammonia through the reactor during H_2SO_4 aerosol generation. The ammonia concentration, as measured by the specific ion electrode, served as an indication of the amount of ammonia that would react with the H_2SO_4. The difference between the formation of ammonium sulfate due to reaction of ammonia with H_2SO_4 and with the various wet and dry adducts was considered to be demonstrative of the increased stability of each of the adducts. It should be remembered, however, that the experiments used concentrations of ammonia that were large compared to environmental conditions. Nominal environmental concentrations would have resulted in the reactivities being much smaller in both cases due to collision probabilities. The results of the above series of tests are given in Table 21. As can be seen from the table, there appears to be little significance in drying the samples.

TABLE 21. PERCENT LOSS OF VARIOUS ADDUCTS DUE TO REACTION WITH AMMONIA

	AAO (%)	Pyridine (%)	DMF (%)	NMF (%)
Wet	69.6	73.1	61.0	97.1
Dried	60.8	77.0	81.1	70.6

MODIFIED THOMAS GENERATOR

Difficulties were continually encountered in obtaining reproducible H_2SO_4 samples at the low μg level using the Thomas flame generator. The Baird generator, while somewhat more reproducible, also had difficulties in that the apparent amount of acid generated could not be accounted for on filter samples. Thus, there was a definite need for an aerosol generator which could be used to obtain a realistic mass balance comparison between predicted aerosol concentration and measured aerosol concentration. In addition, it was felt, based upon previous data, that the new generator should possess the capability of alternately generating aerosols in the size range of both the Thomas and Baird generators. The final generator design consisted of the basic Thomas flame atomizer with the following modifications:

1) Provision was made so that either fuel or compressed air could be passed through the burner orifice, thereby allowing for generation of aerosols in the large or small size range at identical operating pressures.
2) Since the burner tip orifices are extremely critical for maintaining a consistent H_2SO_4 aspiration rate, a Radiometer AutoBurrette, Model ABU-1, was connected to the aspirator and used to feed the H_2SO_4 solution to the orifices in a uniform manner. The delivery rate of the solution into the burner tip was nominally one-half milliter per minute.

The modified Thomas generator in either the flame or flameless mode was used in all subsequent testing.

H_2SO_4 Volatilization Approach (Modified Thomas Generator)

Since it was found that adduct particle size apparently influences the decomposition temperature of the corresponding adduct, it was thought that a possible solution to the H_2SO_4 measurement problem might be to volatilize the H_2SO_4 aerosol. H_2SO_4 is known to volatilize at a temperature substantially lower than the potentially interfering sulfates. The volatilized acid could then be passed through a prefilter which would at the same time collect the unvolatilized sulfur-containing particulates. The volatilized acid could then be reacted on the downstream side of the prefilter and collected on a secondary filter in the absence of interfering particulates. In fact, since the ammonium sulfate salts would be collected on the prefilter, ammonia could be used as the fixing reagent, thereby eliminating possible equilibrium problems between ambient ammonia and the fixing reagents.

To aid in investigating the volatilization approach the aerosol stream from the modified Thomas generator was sampled by two parallel all-Teflon sampling legs. One sampler leg consists of a presection which can be heated, a prefilter, a reaction tube and a final collection filter; the other consists of a presection with no provision for heating, a reactor tube and a final collection filter. Dimensionally, both sample legs are identical. The heated leg of the sample was described on pages 46 and 47. A diagram was presented as Figure 11.

NH_3 Fixing Reagent (Modified Thomas Generator - no flame; both sample legs at ambient temperature)

Since research emphasis shifted to the volatilization of H_2SO_4 and subsequent passage through a prefilter, it was decided that NH_3 should be investigated as a fixing reagent. Theoretically, $(NH_4)_2SO_4$ and other particulates should not pose a problem since they would be stripped from the aerosol stream by the prefilter. The results of these experiments, shown in Table 22, indicate that 54% of the concurrently collected samples had a S_d of less than 0.05 for the individual samples pairs while 23% of the samples had a S_d of less than 0.20 for those sample pairs and 15% of the samples had an S_d of less than 0.31 for each sample pair. All samples were decomposed at 200°C for 15 minutes. Quantitation of these experiments was performed by using the FPD and comparing a known

SO_2 calibration standard with the SO_2 evolved during adduct decomposition. As can be seen from Table 22, the amount of H_2SO_4 found in individual sample pairs was not always in close agreement.

TABLE 22. ANALYSIS OF CONCURRENT SAMPLES USING AMMONIA FIXING REAGENT.

Both Legs of Collection Device at Ambient Temperature

Experiment No.	μg Filter No. 1	μg Filter No. 2	$\overline{X}$	S_d
1	0.48	0.16	0.32	0.23
2	0.58	0.58	0.58	0.00
3	0.40	0.17	0.29	0.16
4	0.47	0.71	0.59	0.17
5	1.0	1.0	1.0	0.00
6	1.0	1.0	1.0	0.00
7	0.78	0.78	0.78	0.00
8	0.48	0.53	0.51	0.04
9	0.91	0.91	0.91	0.00
10	0.56	1.2	0.88	0.45
11	0.70	0.53	0.62	0.12
12	0.69	0.75	0.72	0.04
13	1.2	0.78	0.99	0.30

DEA Fixing Reagent (Modified Thomas Generator - no flame; both sample legs at ambient temperature)

Eight initial experiments were then conducted using diethylamine fixing reagent. The results of these experiments are given in Table 23.

TABLE 23. ANALYSIS OF CONCURRENT SAMPLES USING DIETHYLAMINE FIXING REAGENT

Both Legs of Collection Device at Ambient Temperature

Experiment No.	μg Filter No. 1	μg Filter No. 2	$\overline{X}$	S_d
1	0.52	0.54	0.53	0.01
2	0.23	0.25	0.24	0.01
3	0.36	0.37	0.365	0.01
4	0.34	0.34	0.34	0.00
5	0.30	0.12	0.21	0.13
6	0.44	0.44	0.44	0.00
7	0.29	0.49	0.39	0.14
8	0.50	0.55	0.525	0.04

As can be seen from the table 75% of the values were found to be within ± 5% of the mean value for each sample pair and 25% were within 50% of the mean value for each sample pair. Again, the occasional erratic results were thought to be due to aerosol memory effects in both the generator and sample collection device. In addition, in the case of the DEA adduct, it appeared that heating at 250°C for 15 minutes was not sufficient for complete adduct decomposition.

In order to further examine the perturbations described above, the previous experiments were repeated using ammonia and diethylamine fixing reagents. During these experiments effort was made to insure that the generator had stabilized by collecting a minimum six dummy runs prior to each set of samples. In addition, the decomposition temperature was raised to 300°C for both the ammonia and diethylamine adducts in order to speed up the decomposition process. The results of these experiments are discussed below.

Diethylamine Derivatives (Modified Thomas Generator - no flame; both sample legs at ambient temperature)

It was found that sporadic perturbations of as much as 50 percent occurred between the two legs of the sample collection device even when precautions were taken to insure that the sampling interval was constant and a decomposition temperature of 300°C was used. Further examination of the problem revealed that on occasion the decomposition peaks, as measured by the FPD, tended to tail excessively. It was noted that the tailing phenomenon always worsened toward the latter experiments of the day. Experiments performed using only the decomposition chamber (no sample) during the latter part of the day revealed that considerable sulfur bearing species were still present in the decomposition chamber. In fact, simple insertion of the sample plunger into the decomposition chamber would, on occasion, generate a large response on the FPD as would simply scratching the internal surface of the decomposition chamber. However, after continuous heating of the decomposition chamber at 300°C overnight (it normally remains heated) all traces of residual sulfur bearing species were absent. Results of these tests indicated that the diethylamine derivative was not totally decomposed at 300°C during decomposition periods of approximately five minutes. Thus, at least in part, it appeared that the previous erratic results are due to the diethylamine adduct or intermediate decomposition product collecting on the decomposition chamber walls and sample insertion plunger. The collected material then decomposes sporadically during subsequent analyses. Due to these decomposition insonsistencies of the DEA derivatives emphasis was then focused on NH_3 as the fixing reagent.

Ammonia Derivatives (Modified Thomas Generator - no flame; both sample legs at ambient temperature)

The previous tests using ammonia as the fixing reagent and a decomposition temperature of 200°C also gave sporadic differences of as much as 50 percent between the individual sample collection legs. It was found that raising the decomposition temperature of 300°C resulted in the difference between the individual legs and their mean value on eleven separate runs averaging approximately 7 percent with only one of the runs having a difference of more than 10 percent (13 percent).

The average amount of H_2SO_4 found using ammonia fixing reagent with subsequent thermal decomposition at 300°C and FPD analysis showed that sample leg 1 contained an average of 1.46 μg of H_2SO_4 while sample leg 2 contained an average of 1.38 μg of H_2SO_4. The individual legs were found to agree within 2.8 percent of the mean value for eleven separate runs.

The results of these experiments are given in Table 24 and indicate that duplicate H_2SO_4 aerosol samples can be reproducibly fixed and analyzed at the low $\mu g/m^3$ level, using NH_3 fixing reagent and thermal decomposition techniques. It is apparent from reviewing the data in Table 24 that the generation/collection system had not equilibrated since successive runs clearly show that decreasing amounts of H_2SO_4 were being deposited on the collection filters of both sample legs. This is attributed to the fact that the aerosol generator stack was cleaned prior to the initiation of this series of experiments.

TABLE 24. CONCURRENT AND SEQUENTIAL NH_3 DERIVATIVE SAMPLES

Modified Thomas Generator - No Flame; Both Legs of Collection Device at Ambient Temperature

0.01 N H_2SO_4 Solution Volume Aspirated	Values in μg H_2SO_4 (based on SO_2 evolved)		$\bar{X}$	% Difference from Mean Value
	Leg #1	Leg #2		
1.2 ml	1.70	1.42	1.56	9.0
1.2 ml	1.53	1.18	1.36	13.2
1.2 ml	1.53	1.42	1.48	4.1
1.2 ml	0.92	1.02	0.97	5.2
1.2 ml	1.33	1.18	1.26	6.4
1.2 ml	0.66	0.81	0.74	9.5
1.2 ml	0.61	0.61	0.61	0
1.2 ml	0.55	0.61	0.58	5.2
	$\bar{X}$ 1.10	$\bar{X}$ 1.03	$\bar{X}$ 1.06	2.8
2.5 ml	2.48	2.15	2.32	7.3
2.5 ml	2.13	2.52	2.32	8.6
2.5 ml	2.58	2.31	2.45	5.7
	$\bar{X}$ 2.40	$\bar{X}$ 2.33	$\bar{X}$ 2.36	1.3

ANALYSIS OF CONCURRENT SAMPLES USING THE HEATED SAMPLING DEVICE WITH NH_3 FIXING REAGENT

The logical step after determining that duplicate H_2SO_4 aerosol samples at the low μg level could be collected and analyzed using the dual sample collection device was to determine what effect heating one leg of the collection device might have on reproducibility. This was necessary in order to accurately assess the use of the heated prefilter technique for the elimination of $(NH_4)_2SO_4$ interference. Therefore, a series of experiments was performed in which number one leg of the dual collection device was heated to approximately 105°C while number two leg remained at ambient temperature. It was felt that 104°C was sufficiently hot to volatilize H_2SO_4 aerosol but not decompose $(NH_4)_2SO_4$. In these experiments no filter was inserted in the prefilter holder since the purpose of the tests was to determine if the acid could be heated to volatilization temperature and be quantitatively collected and analyzed. The results are given in Table 25. The average difference between the heated and unheated leg was approximately 7 percent with only two sets of duplicate samples varying by greater than 10 percent (24.6 percent and 13.1 percent). The standard deviation of sequential runs during these tests was approximately 0.33 indicating that the aerosol generator was equilibrated from run to run.

TABLE 25. CONCURRENT AND SEQUENTIAL NH_3 DERIVATIVE SAMPLES WITH NUMBER 1 LEG HEATED (105°C)

Modified Thomas Generator - No Flame

H_2SO_4 Solution Volume Aspirated	Values in µg H_2SO_4 (based on SO_2 evolved) Leg #1 (Heated)	Leg #2	$\overline{X}$	% Difference from Mean Value
2.5 ml	1.53	0.92	1.22	24.60
2.5 ml	2.30	2.14	2.22	3.60
2.5 ml	1.61	1.38	1.49	7.40
2.5 ml	1.61	1.68	1.65	2.10
2.5 ml	1.65	1.61	1.63	1.20
2.5 ml	1.81	1.53	1.67	8.40
2.5 ml	1.32	1.32	1.32	0.00
2.5 ml	1.07	1.38	1.22	13.10
	$\overline{X}$ 1.61	$\overline{X}$ 1.50	$\overline{X}$ 1.55	3.2
Standard Deviation	0.36	0.35	0.33	

It was noted during these experiments that the initial heatup cycle of the heated leg (number 1 side) resulted in a much larger amount of H_2SO_4 aerosol being collected on the heated leg than the unheated leg. This was later shown to be due to H_2SO_4 desorption from the heated sample walls of number 1 leg. This was established by making blank runs without the H_2SO_4 aerosol generator in operation. After approximately five runs the heated sample leg reached equilibrium and gave comparable results. Thus, it appears that the teflon manifold chamber does adsorb some H_2SO_4 which is desorbed when heated. However, it also appears that the walls stabilize relatively quickly to current operating conditions.

MASS BALANCE

Theoretical H_2SO_4 Concentration

Since the values given in Table 2 indicated that the H_2SO_4 generator/sample collection device had reached equilibrium it was decided to attempt a mass balance to determine how theoretical H_2SO_4 values compared to measured aerosol values. The values in Table 24 were not used since they showed a steady downward trend. The aerosol generator stack was cleaned prior to these experiments and it is thought that the stack was re-equilibrating during those experiments.

The lineal flow through the aerosol generator stack was measured with a hot wire anemometer and found to be 950 ft/min and the cross section area of the stack had a diameter of 4.25 in. This corresponds to a total volume flow of 9.93 m^3 per sample run. During the course of a run (3.8 min), 2.5 ml of a 0.01 N H_2SO_4 solution was aspirated into the aerosol generator stack which corresponds to a predicted aerosol concentration of 123 μg H_2SO_4 per cubic meter of air.

Measured H_2SO_4 Concentration

The average weight of H_2SO_4 found on the collection filters as shown in Table 25 was 1.55 μg. Since the volume of aerosol stream sampled was consistently 42 liters (1.5 ft^3) this corresponds to a measured aerosol concentration of 36.9 $\mu g/m^3$ or approximately one third of the 123 $\mu g/m^3$ aerosol concentration predicted.

It had been expected that $(NH_4)_2SO_4$ would thermally decompose at 300°C to evolve SO_2 in a stoichiometric ratio of one mole of SO_2 evolved for each mole of $(NH_4)_2SO_4$. However, previous studies with acetaldoxime and diethylhydroxylamine H_2SO_4 adducts had shown that they thermally decompose to evolve SO_2 in a stoichiometric ratio of one to three and one to two, respectively. Therefore, since the exact stoichiometric release of SO_2 from $(NH_4)_2SO_4$ had not previously been established experiments were performed to determine the amount of SO_2 evolved from a known amount of $(NH_4)_2SO_4$.

Twenty microliters of a 0.001 M $(NH_4)_2SO_4$ solution were deposited by micropipet onto the surface of several Mitex filters. The filters were then thermally decomposed individually at 300°C and the amount of volatile sulfur species evolved measured with the Flame Photometric Detector. Based on a standard SO_2 calibration curve, derived by injecti known SO_2 gas mixtures into the decomposition chamber, it was determined that 0.44 and 0.43 µg of SO_2 were being evolved from the respective filters. Twenty microliters of a 0.001 M $(NH_4)_2SO_4$ solution contains 2.64 µg of $(NH_4)_2SO_4$. Assuming that each mole of $(NH_4)_2SO_4$ decomposed to give one mole of SO_2 we would expect to find

$$2.64 \times \frac{64}{132} = 1.28 \ \mu g \text{ of } SO_2$$

evolved from the samples. However, an average of 0.435 µg were evolved from the known samples resulting in a stoichiometric ratio of

$$\frac{1.28 \ \mu g \ SO_2 \text{ predicted}}{0.435 \ \mu g \ SO_2 \text{ evolved}} \text{ or } \frac{3}{1}$$

Thus, each mole of $(NH_4)_2SO_4$ produces one third mole of SO_2 when thermally decomposed at 300°C. Therefore, the values given in Table 25 should be multiplied by 3 since they were calculated assuming a one to one stoichiometric relationship between SO_2 evolution and the amount of $(NH_4)_2SO_4$ present. The concentration of H_2SO_4 aerosol in the sample then becomes 111 µg H_2SO_4/m^3 which is close to the theoretical value of 123 µg H_2SO_4/m^3. The higher aerosol concentration was used in order to shorten the required sampling time. The results of these experiments are summarized in Table 26.

TABLE 26. COMPARISON OF PREDICTED AND MEASURED AEROSOL CONCENTRATIONS

Predicted H_2SO_4 Aerosol Concentration	123 µg/m^3
Measured H_2SO_4 Aerosol Concentration using NH_3 Fixing Reagent and Thermal Decomposition at 300°C	111 µg/m^3

VOLATILIZATION OF H_2SO_4 (Modified Thomas Generator)

Results of initial tests to determine the volatilization of H_2SO_4 with subsequent passage through the prefilter are shown in Table 27. These data reflect the relative efficiency of the volatilized acid to pass through the prefilter and to be collected on the sample collection filter at various temperatures. The aerosol samples were prepared using 0.01 N H_2SO_4 which corresponds to a predicted aerosol concentration in the generator of 123 μg H_2SO_4 per cubic meter of air. Under these conditions, the maximum amount of H_2SO_4 which could be sampled, representing 100% sampling efficiency, is 4.48 μg. The total amounts sampled range from 4.31 μg (96%) to 1.05 μg (23%). The average collection efficiency for all tests is 53%, while the average for the low temperature tests was 68%

TABLE 27. PERCENT OF ACID PASSING PREFILTERS (123 μg/m^3)

(Modified Thomas Generator - No Flame)

Temperature of Prefilter, °C	Sample Flow l/min	Total μg H_2SO_4 Prefilter + Collection Filter	% of Total Collection Filter	Measured H_2SO_4 Aerosol Concentration (μg/m^3)
57	9.8	2.90	17	69.0
		1.99	16	47.4
70	9.8	3.95	18	94.0
		2.53	13	60.2
		3.92	14	93.3
108	9.8	4.31	40	103.0
		1.61	35	38.3
		1.05	54	25.0
		1.04	54	24.8
155	6.0	2.20	59	52.4
		3.82	70	90.9
		1.47	86	34.9
		1.25	81	29.8
		3.87	84	92.1
		2.20	59	52.4
		1.45	70	34.5
		1.13	62	26.9

Collection of H_2SO_4 Aerosol in the 10 μg/m^3 Range (Modified Thomas Generator-No Flame)

The data presented above for the collection efficiency of sulfuric acid are based upon the assumption that sulfur interference levels in the laboratory are a minor interference when the samples generated are in the 123 μg/m^3 range.

The next series of experiments was devised to duplicate the above results at a tenfold reduced concentration. At 12.3 μg/m^3 sample generation, however, ambient sulfur constituents or ammonia might be a major interference. Therefore, two preliminary experiments were performed to determine this effect.

First, the experiments with H_2SO_4 volatilization (123 $\mu g/m^3$) at high temperature were repeated, but at 200°C. At this temperature, the maximum amount of H_2SO_4 collected on the sample collection filter was 89% of the total and the average amount was 78% of the total. The total collection efficiency was 44% compared to 48% for the tests made at 155°C. This experiment confirmed the previous tests, establishing a maximum volatilization coefficient, again assuming $(NH_4)_2SO_4$ is not an interference.

The second experiment was designed to insure that minimum ammonia and ambient surfate interference from the laboratory environment was achieved. Only after this was determined could the low level H_2SO_4 volatilization be attempted. Three types of samples were used to determine nominal background sulfate interference levels. The three samples consisted of blank unused filters (Mitex LS), filters through which untreated laboratory air passed up the aerosol generator stack, and filters through which treated (filtered and H_3PO_4 scrubbed) laboratory air was passed up the aerosol stack. All samples were subjected to thermal decomposition at 300°C with subsequent FPD detection. The results of these experiments are given in Table 28.

TABLE 28. BACKGROUND SULFUR LEVELS AS μg of H_2SO_4

Blank Filters	Treated Air (1.5 ft^3)	Untreated Air (1.5 ft^3)
0.01 to 0.14 μg	0.15 to 0.19 μg	0.21 to 0.55 μg

The individual values vary from day to day with typical values for untreated air being from 0.24 to 13.1 $\mu g/m^3$ (as the equivalent amount of H_2SO_4 required to give the measured background response). Thus, it appears that background levels of sulfur-containing species would be a significant factor when compared to the theoretical concentration of 12.3 $\mu g/m^3$ H_2SO_4 aerosol. The treated air, which was normally used for actual experiments gave a maximum background equivalence response of 4 to 5 $\mu g/m^3$ H_2SO_4.

Whether treated or untreated air is sampled, the FPD response is proportional to the amount of air sampled; however, the μg amounts are uniformly less for H_3PO_4-treated, filtered air than for the untreated air at ambient conditions. Thus, it appeared that the air scrubber system removed a large portion of the background sulfur-containing constituents, but that the remainder is still significant when compared to aerosols generated at the 12.3 μg/m^3 level. It appeared, however, that the residual sulfur species might be the result of the H_2SO_4 generator stack gradually evolving sporatic amounts of H_2SO_4 aerosol previously adsorbed to the stack walls.

Collection of H_2SO_4 Aerosol in the 12.3 μg/m^3 Range (Modified Thomas Generator - No Flame)

As stated previously, it was expected that residual sulfur species would be a significant interference at low levels of H_2SO_4 collection. After allowing for background levels the values given in Table 29 were obtained at ambient conditions.

TABLE 29. ANALYSIS OF H_2SO_4 AEROSOL AT THE 12.3 μg/m^3 LEVEL. (AMBIENT CONDITIONS)

Total μg H_2SO_4	Measured H_2SO_4 Aerosol Concentration μg/m^3
0.66	15.8
0.44	10.5
0.74	17.6

The maximum amount of H_2SO_4 to be expected on the filters, based upon the operating conditions of the generator, was 0.53 μg as H_2SO_4. Background samples (taken before each sampling) ranged from 0.01 μg (as SO_2) to 0.25 μg.

An additional series of experiments in the 12.3 μg range using the heated zone to volatilize the aerosol resulted in findings which paralleled those obtained with the 123 μg/m^3 aerosol. The results of these experiments, after correcting for background levels, are given in Table 30.

Collection of H_2SO_4 Aerosol Tests in the 61 μg/m^3 Range (Modified Thomas Generator - No Flame)

Several experiments were run at an intermediate aerosol concentration range to determine if the H_2SO_4 collection efficiency dropped with increasing volatilization temperature. The results of these experiments are shown in Table 31.

TABLE 30. HEATED AEROSOL COLLECTION AT THE 12.3 μg/m^3 LEVEL (SAMPLE RATE 9 l/min)

Temperature of Heated Leg, °C	Total μg H_2SO_4 Prefilter and Collection Filter	% on Collection Filter	Measured H_2SO_4 Aerosol Concentration, μg/m^3
20	0.37	0	8.8
110	0	0	0
110	0	0	0
110	0	0	0
20	0.42	0	10.0

TABLE 31. HEATED AEROSOL COLLECTION AT THE 61 μg/m^3 LEVEL (SAMPLE RATE 9 l/min)

Temperature of Heated Leg, °C	Total μg H_2SO_4 Prefilter and Collection Filter	% on Collection Filter	Measured H_2SO_4 Aerosol Concentration, μg/m^3
20	2.75	0	65.4
50	2.11	21	50.2
110	1.65	0	39.3
110	1.65	0	39.3
125	1.22	36	29.0
125	1.70	38	40.5
145	0.32	68	7.6
145	0.74	86	17.6
145	0.13	100	4.1

Since it was previously shown that H_2SO_4 could be heated to 105°C and collected with an average efficiency of 90.2% when a prefilter was not used, it appeared that the prefilter had a detrimental effect on total collection efficiency. It was thought that the poor collection efficiency might be attributable to the gas stream being cooled too much and the reaction tube acting as a thermal precipitation or adsorption surface. When samples are taken under ambient conditions or, in the case of the treated tests, when only one filter is in place, the vacuum pump operates continuously, as does the preheater. When two filters are in place, however, it is necessary to shut down the pump momentarily while removing and analyzing each of the two filters. This causes fluctuations in the wall temperature and possibly the adsorption/desorption of H_2SO_4 from the sample walls.

Modification of Sampling Device

Heated Reaction Tube --

Normally, the fixing chamber was heated by the gases passing through the preheated section. The fixing chamber runs at approximately 50 to 60°C, while the preheater can be operated up to 180°C. In order to narrow the temperature differential between the two sections, the fixing chamber was wrapped with four feet of glass-backed heating tape and insulated with fiberglass pipe cover. The heating tape was controlled by a Variac.

Reagent Addition Tubes --

Previously all gaseous fixing reagents were added to the reaction chamber through a single Teflon side arm. At this time, three additional Teflon side arms were added to the fixing chamber to aid in establishing turbulent flow. All Teflon side arms were spaced equidistant around the reaction chamber tube, approximately 4 cm below the prefilter.

Electrostatic Charge --

It was postulated that electrostatic charge accumulation might be responsible for the sporatic perturbation of data from identical samples. Therefore, it was decided to modify the Teflon sample tube so that static charge build up might be prevented. This was attempted by placing three 0.005 cm gold plated (1%) tungsten wires along the inside walls of both the preheater and fixing chamber. The wires were spaced equidistant and each wire exited the tube through small holes at each end of the respective tubes. The wires were held in place by screws partially inserted into the wire exit holed. In addition to the above modifications, the Teflon tube used to transfer the aerosol stream from the aerosol generator to the sampler was replaced with a 1.25 cm O.D. stainless steel tube. The gold wires in each sampler section and the stainless steel sample tube were tied together and grounded.

Effect of Sampler Modifications (Modified Thomas Generator - No Flame)

Since previous experiments at ambient temperatures had shown occasional perturbations, a series of experiments was run to determine if the above modifications had reduced their frequency and magnitude. Table 32 shows the results of a series of eight samples collected at the prefilter, while Table 33 shows the results of eight samples deposited at the collection filter. All samples taken from the collection filter were fixed in the reaction chamber with NH_3 obtained from a bubbler device containing NH_4OH. Samples obtained at the prefilter were removed from the sampler and immediately fumed over concentrated NH_4OH. All samples were thermally decomposed at 300°C and the decomposition products passed through the Flame Photometric Detector. All samples were collected on Mitex filters while the FPD was calibrated with SO_2 mixtures.

TABLE 32. ANALYSIS OF SAMPLES TAKEN AT THE PREFILTER (Modified Thomas Generator - No Flame)

Sample No.	$\mu g\ H_2SO_4$ Per Filter	$\mu g\ H_2SO_4/m^3$	% Difference From Mean
1	3.03	216	+2.4
2	3.52	251	+18.9
3	2.76	197	-6.6
4	2.76	197	-6.6
5	2.79	199	-5.7
7	2.76	197	-6.6
8	3.21	229	+8.5
		$\overline{X}$ 211	

$S_d = 19.9$

TABLE 33. ANALYSIS OF SAMPLES TAKEN AT THE COLLECTION FILTER (Modified Thomas Generator - No Flame)

Sample No.	µg H_2SO_4 per Filter	µg H_2SO_4/m^3	% Difference From Mean
1	2.66	190	-18.1
2	3.55	253	9.0
3	3.18	227	-2.2
4	3.68	263	+13.4
5	2.94	210	-9.5
6	3.18	227	+2.2
7	3.25	232	0.0
8	3.52	251	+8.2
		$\bar{X}$ 232	
		$S_d = 24.1$	

As can be seen from Table 32, all samples taken at the collection filter except Number 2 gave results that were well within 10% of the mean value of 211. The standard deviation for this series of experiments was 19.9, which is within 10% of their mean value. Table 33 shows that samples collected at the prefilter location were generally within 10% of their mean value of 232 except for Runs 1 and 4. The standard deviation for this series of tests was 24, which is approximately 10% of the mean value. Previously reported experiments performed at ambient conditions using the unmodified sampler gave standard deviations which were 43% and 23% of their mean values. Thus, substantial improvement at the 100 µg/m^3 concentration is evident due to the sampler modifications. It is felt that the few perturbations found in the results reported here are due to residual electrostatic accumulation. The total elimination of this effect would probably require the use of a nuclear static eliminator.

It should be noted that the results obtained from the two series of data discussed here were obtained on two different days. Thus, the aersol generation and sampling systems were totally shut down between the two series of tests. Considering that the mean results of each series of experiments agree to within ten percent of the other, this suggests a high degree of reproducibility for the aerosol generator, the sampling methodology and the analytical technique used to quantitate the results.

Volatilization of H_2SO_4 Aerosol at 145°C (Modified Thomas - No Flame)

Several experiments were performed to determine if H_2SO_4 aerosol could be passed through a Mitex LS filter at 145°C. The results of these experiments, given in Table 34, show that at 145°C the average slip through the prefilter is 20%. Thus, it appears that H_2SO_4 droplets on the order of 1 to 5 μm are not efficiently volatilized at 145°C.

TABLE 34. H_2SO_4 SLIP THROUGH PREFILTER AT 145°C
(Modified Thomas Generator - No Flame)

Total μg H_2SO_4 Recovered	μg H_2SO_4 Prefilter	μg H_2SO_4 Collection Filter	% Slip Through Prefilter
2.54	1.76	0.78	31
2.57	2.27	0.32	12
2.30	1.90	0.41	18

An experiment was performed at 145°C in which the acid collected on the prefilter was exposed to an additional five minutes of the 145°C gas stream passing through the filter (no H_2SO_4 aerosol in the stream). Results of this experiment showed that approximately 50% of the H_2SO_4 collected had slipped the prefilter. This explains why varying the total flow through the sampler in previous experiments from 9.8 l/min to 4.8 l/min did not substantially affect the volatilization efficiency. It is apparent that the larger aerosol droplets cannot be efficiently volatilized at nominal reactor lengths (30 cm), sampler flow rate (1 to 10 l/min) or preheater temperature (145°C) prior to collection on the prefilter. The advantage of this approach was to have the H_2SO_4 volatilized before reaching the prefilter, rather than having the acid slowly boil off the prefilter. It must, however, be remembered that in environmental samples, the larger aerosol droplets would probably have been neutralized by other ambient constituents (NH_3, etc.) prior to their growth into this size range.

Quantitative Recovery of Volatilized H_2SO_4 (Modified Thomas Generator)

Previous tests to investigate the volatilization of H_2SO_4 have shown that up to 75% of the total acid sample was lost when the acid passed through the prefilter. It was suggested that these losses were due to the combined effects of temperature differential between the preheater and fixing portions of the sampler and electrostatic accumulation. Therefore, since the sampler was modified to reduce the above effects, a series of experiments was performed to determine if any improvement was obtained. The results of these tests (shown in Table 35) indicate that ≈100% of the acid passing through the prefilter was quantitatively recovered on the collection filter. A comparison of results in Table 34 with those in Tables 31 and 32 shows that the mean value for this series of experiments agrees with their mean values within 5%. The standard deviation of this series of experiments was 13.1 which was within 6% of the mean value. Thus, considerable improvement is evidenced by the modifications made to the sampler. Prefilter slip, however, was still not sufficient to suggest that the technique was not acceptable for aerosols where total sample size is in the low µg range.

TABLE 35. QUANTITATIVE RECOVERY OF H_2SO_4 PASSED THROUGH THE PREFILTER (Modified Thomas Generator)

Total µg H_2SO_4	µg H_2SO_4 Prefilter	µg H_2SO_4 Filter	µg H_2SO_4/m^3	% Difference From Mean
2.54	1.76	0.78	227	+2.7
2.57	2.27	0.32	230	+4.1
2.30	1.90	0.41	206	-6.8
			$\bar{X}$ 221	
			S = 13.1	

H_2SO_4 Aerosol Volatilization at 190°C (Modified Thomas Generator - With Flame)

In order to study H_2SO_4 droplets in the 0.1 to 0.5 µm size range, the modified Thomas generator was changed to the flame mode of operation. It was thought that the slip efficiency problem might be associated with the relatively large aerosol droplet size being studied (1 to 5 µm). A decision was made that smaller H_2SO_4 droplets might be volatilized more readily and thus pass through the prefilter efficiently. To determine if this were true, a series of experiments was performed. The results of these experiments are given in Table 36 and show that at 190°C even H_2SO_4 droplets in the 0.1 to 0.5 μm range do not pass through the prefilter efficiently.

TABLE 36. PASSAGE OF H_2SO_4 DROPLETS THROUGH PREFILTER AT 190°C (Modified Thomas Generator - with Flame)

Total H_2SO_4 (μg)	H_2SO_4 Prefilter	H_2SO_4 Collection Filter	% Slip Prefilter
8.6	6.7	1.9	22.1
8.9	7.2	1.8	20.2

H_3PO_4 Scrubbed Aerosol Generator Diluent Air (Modified Thomas Generator - with Flame)

Since the difficulty was observed in passing the H_2SO_4 aerosol through the prefilter at 190°C, to insure that ambient ammonia was not reacting with the aerosol before it reached the prefilter, several experiments were performed in which the aerosol diluent air was passed through an H_3PO_4 scrubber consisting of a 9 cm O.D. x 10 cm length of phosphoric acid coated quartz chips connected to the inlet of the diluent air pump. As can be seen from Table 37, no significant improvement was noted in the percentage of H_2SO_4 passed through the prefilter as a result of using the phosphoric acid scrubber. Thus, it appeared that ambient ammonia was not reacting with the H_2SO_4 aerosol prior to reaching the prefilter.

TABLE 37. PASSAGE OF H_2SO_4 DROPLETS THROUGH PREFILTER USING H_3PO_4 SCRUBBED AIR (Modified Thomas Generator - With Flame)

Total H_2SO_4 (μg)	H_2SO_4 (μg) Prefilter	H_2SO_4 (μg) Collection Filter	Percent Slip	Prefilter Temp.(°C)
7.5	6.7	0.78	11	144
7.9	7.1	0.78	10	177

H_2SO_4 Aerosol Volatilization at 190°C for Extended Period (Modified Thomas Generator - With Flame)

Several experiments were performed in which preheated air (190°C) was allowed to pass over collected sulfuric acid samples for extended periods. The purpose of these tests was to determine the relative time necessary for the H_2SO_4 collected on the filter to volatilize off the prefilter and pass through the collection filter. As can be seen from Table 38, substantially more H_2SO_4 passed through the prefilter when heated for an additional 15 to 25 minutes. These experiments indicated that extended periods were necessary to volatilize H_2SO_4 aerosols in the 0.1 to 0.5 µm size range at a prefilter temperature of 190°C.

TABLE 38. PASSAGE OF H_2SO_4 DROPLETS THROUGH PREFILTER AT 190 °C VERSUS TIME (Modified Thomas - with Flame)

Total H_2SO_4 (µg)	H_2SO_4 (µg) Prefilter	H_2SO_4 (µg) Collection Filter	% Slip	Post-Heating Time (min)
8.8	6.9	1.9	21.6	0
10.7	6.2	4.5	42.0	15
9.6	6.1	3.5	36.4	25

Cabot H_2SO_4 Aerosol Analyzer

The Cabot H_2SO_4 Aerosol Analyzer, which works on the principle of volatilizing H_2SO_4, uses ultra-dry air and elevated temperatures to bring about the complete vaporization of H_2SO_4 droplets over a period of 15 minutes. Based on Cabot's results, it appears that a low ambient relative humidity is necessary to efficiently volatilize the H_2SO_4 aerosols. Since it was known that the humidity of our aerosol generators runs approximately 100%, this could be the source of the difficulties. It was, therefore, planned to use the animal chambers (ultrafine H_2SO_4 aerosol) at the Health Effects Research Laboratory (HERL) to study the volatilization of H_2SO_4. The use of the animal study chambers would enable the generation and control of the H_2SO_4 aerosol of known size (<0.1 µm) in an environment of controlled humidity. These studies would show whether even at low relative humidity, the acid would pass the prefilter.

FIELD TESTS

Several field tests were conducted in order that the Atlantic Research gas phase fixation/analysis concept might be compared with other available H_2SO_4 collection/measurement techniques. Animal test chambers located within the Health Effects Research Laboratory (HERL) at the Environmental Protection Agency, Research Triangle Park, North Carolina, were used for the first series of field tests. The second series of field tests consisted of actual enviornmental samples taken in locations of anticipated varying sulfuric acid aerosol levels. Each series of field tests is discussed in the following sections.

Animal Chamber Field Tests

The H_2SO_4 aerosol animal chamber used for these studies was located in the Health Effects Research Laboratory of the Environmental Protection Agency at Research Triangle Park, North Carolina. The chamber was approximately 0.5 M wide x 0.5 M wide x 5.0 M long. The entire chamber was constructed of plexiglass and had plexiglass tubular inserts protruding into the main chamber area. The tubular inserts were used for exposing animals to the H_2SO_4 aerosol stream. The chamber was designed to operate with a constant aerosol droplet size of approximately 0.01 to 0.08 μm (ultrafine), an aerosol concentration of approximately 500 $\mu g/m^3$ and a relative humidity of approximately 50%. In addition, the chamber was fully instrumented to observe in situ any sudden perturbations in the H_2SO_4 droplet size (mobility particle analyzer), H_2SO_4 droplet concentration (Monitor Lab Sulfur Analyzer) and the relative humidity (Humidity Monitor). It was felt that a closely controlled environmental system such as the animial test chamber would allow for a much more accurate initial assessment of the gas phase fixation concept than general environmental sampling. This was considered to be the case since there was no viable H_2SO_4 analysis referee method suitable for precise field comparison. It was recognized that the operating aerosol level of the animal chamber was considerably higher than anticipated environmental levels, but it was felt that the positive aspects of the closely controlled animal chamber environment outweighed the negative aspect of the higher aerosol concentration.

The objectives of the animal chamber studies at HERL were to investigate the following:

1) Prefilter slippage efficiency of H_2SO_4 droplets at various temperatures in a controlled humidity environment.
2) H_2SO_4 adduct decomposition characteristics.
3) Quantitative comparison of Environmental Protection Agency and Atlantic Research results on identical samples.
4) $(NH_4)_2SO_4$ interference.
5) Storage studies.

Sensitivity Studies --

During the animal chamber studies at HERL, an effort was made to collect and analyze samples on site. Analysis of these samples required the use of the Environmental Protection Agency's Bendix Total Sulfur Analyzer. Initial experiments using the Bendix Total Sulfur Analyzer connected to Atlantic Research's thermal decomposition chamber showed that at 500 μg H_2SO_4/m^3 (5 minute sample collection period), a 10 liter sample saturated the Bendix detector. A second series of runs was made with a sample collection time of one minute (2 liters) which also resulted in detector saturation. Adjustments to the photomultiplier head voltage and the electrometer did not significantly increase the dynamic range of the Bendix Total Sulfur Analyzer. Calibration curves obtained on the Bendix Total Sulfur Analyzer using SO_2 standards showed that this detector was approximately ten times more sensitive than the Melpar FPD which had been utilized at Atlantic Research. Thus, the increased sensitivity of the Bendix Total Sulfur Analyzer, coupled with the larger H_2SO_4 loading ($\approx$500 $\mu g/m^3$) necessitated that the samples be returned to Atlantic Research for analysis. Since this possibility had been anticipated, provision had been made to return the samples in plastic Petri dishes.

From the above calibrations, it was determined that the sensitivity of the combined Atlantic Research decomposition chamber/Bendix Total Sulfur Analyzer was on the order of 0.01 μg H_2SO_4. Based on the original program requirement of 0.25 μg H_2SO_4/m^3, it would require a sample of 40 liters to obtain a sufficient quantity to be detected.

H_2SO_4 Prefilter Slippage --

Studies were performed at several prefilter temperatures in order to determine the temperature at which H_2SO_4 aerosol sampled from the animal chambers might pass through the prefilter. The device, shown in Figure 11 (page 47) was used during these studies and was designed to raise the temperature of the aerosol sample stream sufficiently to volatilize H_2SO_4. The device consisted of a 30 cm x 1.8 cm I.D. heavywall Teflon tube heated by glass-backed tape. At the end of the 30 cm heated section was a Fluoropore prefilter which allowed the volatilized acid to pass while collecting the remaining particles. Once through the prefilter, the volatilized acid was mixed with fixing reagent in a 15 cm Teflon mixing chamber. The adduct was then collected on a second Fluoropore filter at the end of this 15 cm section. The fixing chamber was also wrapped with a glass-backed heating tape and insulated in order to accurately control temperature.

Animal chamber experiments were performed using the above apparatus with prefilter temperatures ranging from 95 to 132°C. The flow rate through the sampler was held at 2.2 liters/minute using a critical orifice with all samples being collected for exactly two minutes. After collection, the samples were stored in plastic Petri dishes for shipment to Atlantic Research for analysis. Prefilter samples were manually fixed with NH_3 by fuming prior to being stored in the plastic Petri dishes. Final filter samples were fixed _in situ_ in the fixing chamber prior to collection.

The results of these experiments are given in Table 39. The temperature at both the prefilter and the collection filter are given in the table, as well as the temperature midway between the sampler inlet and the prefilter and midway between the prefilter and the collection filter. As can be seen from the table, the largest H_2SO_4 concentration, 33.5%, occurred with a prefilter temperature of 95°C. The data trend suggests that the lower prefilter temperature allows the H_2SO_4 aerosol to pass the prefilter more efficiently. This is somewhat perplexing since it was thought that the higher temperatures would cause the acid aerosol to slip the prefilter more readily. Unfortunately, temperatures below 95°C at the prefilter were not investigated. In any case, none of the results suggest the efficient transport of volatilized H_2SO_4 through the prefilter.

TABLE 39. ANIMAL CHAMBER TESTS (PREFILTER AND COLLECTION FILTER)

Sample No.	Preheater Tube Temp. Midway to Prefilter	Preheater Tube Temp. At Prefilter	Collection Tube Temp. Midway to Collection Filter	Collection Tube Temp. At Collection Filter	µg H_2SO_4 Filter	Percent Prefilter Slippage
1 Prefilter	157	96			1.69	29.9
2 Collection			80	65	0.72	
					2.41	
2 Prefilter	168	95			2.02	33.5
2 Collection			65	55	1.02	
					3.04	
3 Prefilter	167	108			3.04	7.2
3 Collection			72	60	0.22	
					3.26	
4 Prefilter	168	110			2.19	9.1
4 Collection			70	60	0.22	
					2.41	
5 Prefilter	190	126			2.25	14.8
5 Collection			80	64	0.39	
					2.64	
6 Prefilter	198	132			2.65	12.8
6 Collection			80	66	0.39	
					3.04	

Thermal Decomposition Studies --

These studies were performed to evaluate fixing reagents and their corresponding adducts rather than H_2SO_4 volatility. Three different H_2SO_4 fixing reagents were used during these experiments in the HERL animal chambers in order to determine the decomposition temperatures of the corresponding adduct formed from ultrafine (∿0.05 μm) H_2SO_4 aerosol. The reagents used for these studies were acetaldoxime, N-methylformamide and ammonia. Ammonia was used as a fixing reagent to determine the effect of $(NH_4)_2SO_4$ interference on the other two adducts. The three fixing reagents and their corresponding adducts are discussed below. It should be noted that all samples were taken at ambient temperature with no prefilter installed at the end of the volatilization chamber.

$(NH_4)_2SO_4$ Studies -- Two series of experiments were conducted during this study. The first series of experiments involved fixing the H_2SO_4 aerosol with ammonia during the collection process, while the second series involved waiting approximately 10 minutes before NH_3 fixation. Sufficient samples were collected during each series so that thermal decomposition information could be obtained at several temperatures. The purpose of these studies was twofold: (1) to determine the decomposition temperature of $(NH_4)_2SO_4$ formed from ultrafine (0.05 μm) H_2SO_4 droplets; and (2) to determine the effect on decomposition temperature when the H_2SO_4 droplets were allowed to age an additional 10 minutes prior to forming $(NH_4)_2SO_4$. The data from these experiments, shown graphically in Figures 29 and 30, indicate that there is very little, if any, difference in the amount of SO_2 evolved at a given decomposition temperature by either method of NH_3 fixation. It should be noted however, that the relative humidity within the animal chambers was on the order of 40%, so that the aerosol droplet growth rate was somewhat inhibited. It appears from the data shown in Figure 30 that the H_2SO_4 fixed with ammonia ten minutes after sample collection begins to decompose at a temperature of approximately 185°C. Unfortunately, no decomposition data was obtained between 170° and 196°C for the H_2SO_4 aerosol droplets fixed immediately with ammonia during sample collection. At 170°C, however, there was no sign of sample decomposition.

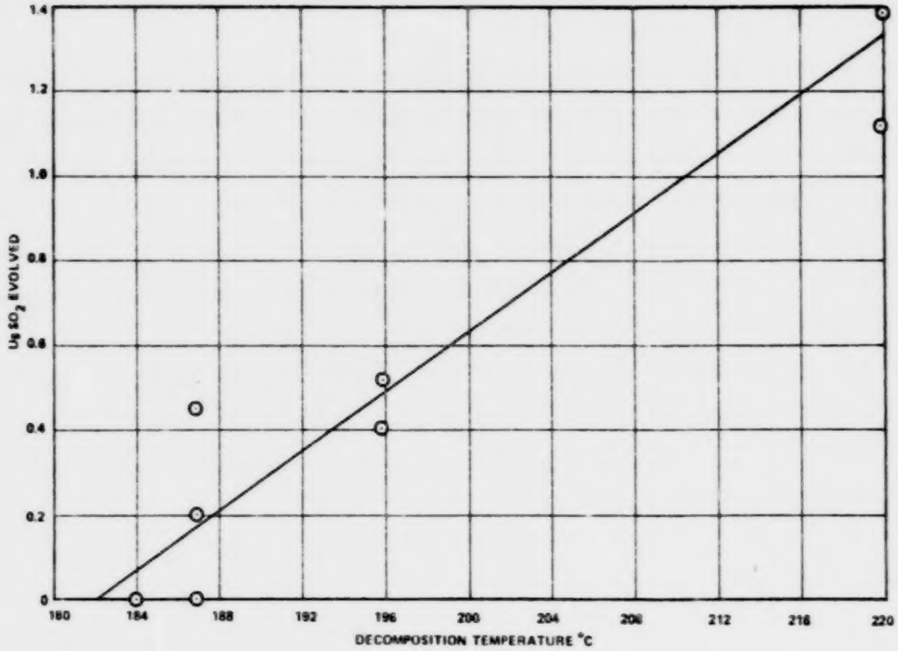


Figure 29. Submicron particles fixed with ammonia ten minutes after sample collection.

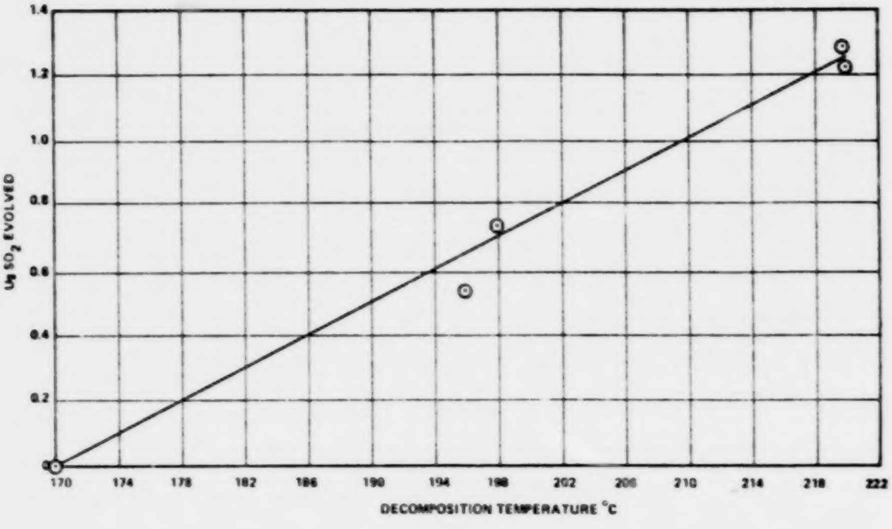


Figure 30. Submicron particles fixed with ammonia during sample collection.

NMF/AAO Studies -- Several aerosol samples were reacted with N-methyl formamide and acetaldoxime in order to determine the decomposition temperature of the associated adducts. The results of these experiments are shown in Figures 31 and 32.

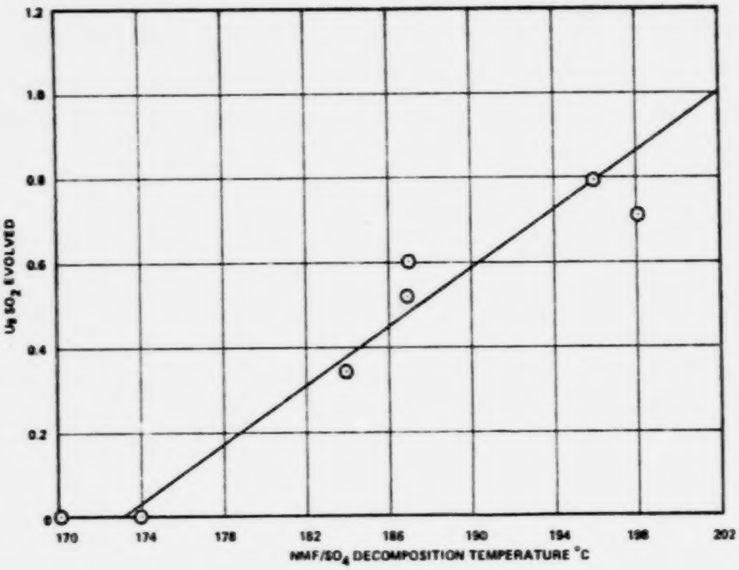


Figure 31. Decomposition profile of NMF-SO$_4$ adduct.

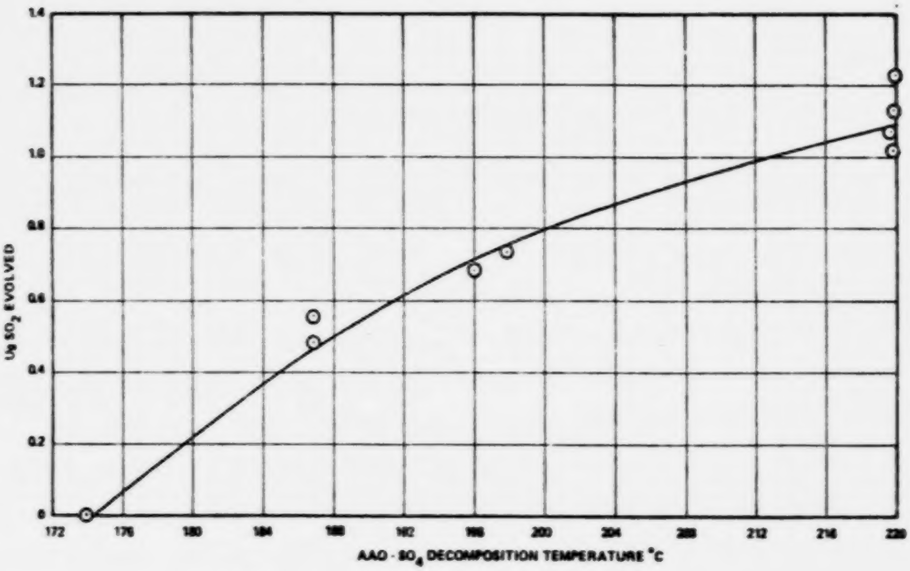


Figure 32. Decomposition profile of AAO-SO$_4$ adduct.

As can be seen from the figures, at 174°C neither the NMF nor the AAO adducts decompose, while at 184°C significant decomposition appears to take place. Thus, it would seem that the temperature range between 174°C and 184°C is of primary importance since the $(NH_4)_2SO_4$ experiments indicated that it did not decompose until approximately 185°C. A composite curve of $(NH_4)_2SO_4$, AAO-SO_4 and NMF-SO_4 is shown as Figure 33. It appears from the composite curve that there may be sufficient difference in decomposition temperatures to allow for the selective decomposition of the AAO/NMF adducts in the presence of $(NH_4)_2SO_4$.

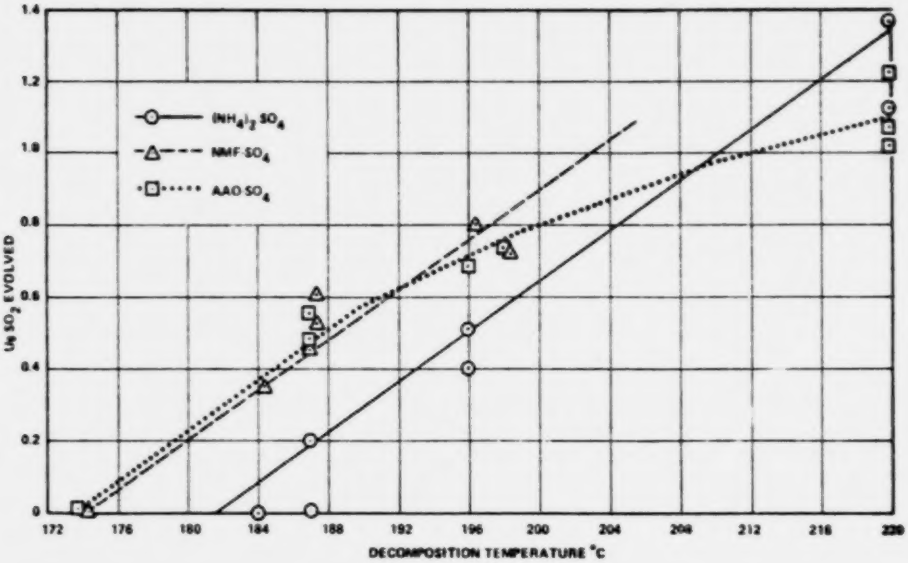


Figure 33. Composite decomposition profile - AAO-SO_4, NMF-SO_4, $(NH_4)_2SO_4$.

Quantitative Comparisons--

Samples were taken from the HERL Animal Chambers on July 19 and 20, 1978, for quantitative comparison between the gas phase fixation/thermal decomposition technique, the EPA procedure (thorin), and the *in situ* Monitor Labs Sulfur Analyzer. The Environmental Protection Agency (EPA) and Atlantic Research Corporation (ARC) samples were taken on Milipore FH filters, 0.5 µm pore size. The ARC samples were fixed during sample collection, removed from the sampler and immediately placed in plastic Petri dishes for shipment to ARC. The EPA samples were immediately placed in a solution of 5X10^{-5} N perchloric acid for stabilization purposes. The Monitor Labs Sulfur Analyzer was a continuous analyzer, and therefore required no sample storage.

The ARC results from all samples taken on July 19 are included in Table 40, while the results from all the quantitative samples taken on July 20 are given in Table 41. As can be seen from the two tables, the average daily values obtained by ARC were within 10% of one another. During the course of this sampling, EPA obtained concurrent samples for analysis by the thorin technique. The results of the EPA thorin analysis are shown in Table 42, along with the ARC results from the pertinent samples and the real time total sulfur analyzer reading. Table 43 is a summary of the individual results given in Table 42 and reflects the daily averages for both ARC and EPA data.

It is interesting to note in Table 42 that the FPD data suggest that no sudden H_2SO_4 perturbations occurred in the animal chamber during these tests. It, therefore, seems logical that the data from EPA samples 33-138, 33-139, 33-145 and 33-147 are low. This is further substantiated by the ARC data which suggests that the H_2SO_4 concentration was not halved during the sampling period. The fact that both sets of data reflect one half of the H_2SO_4 aerosol concentration previously determined by both the other EPA results and the ARC results suggests the possibility of a 2:1 dilution error during the chemical analysis.

If the questionable samples are deleted from the sample matrix and the remaining data averaged for each of the two days, the comparisons given in Table 44 are obtained. These results show that on 7/19/78 the EPA and ARC results agreed to within 8%, while on 7/20/78, the data agreed to within 14%. The results also suggest that very little, if any, ARC sample loss occurred during a one-month storage period between sample acquisition and analysis. The samples were kept refrigerated in the original Petri dishes during this period.

Environmental Field Tests

Samples were taken from two locations for this series of experiments. Two sets of samples were taken in a rural location of the Shenandoah Valley

TABLE 40. ANIMAL CHAMBER STUDIES - ALL QUANTITATIVE SAMPLES TAKEN BY ARC ON 7/19/78

ARC Sample No.	Time of Sampling	$\mu g\ H_2SO_4/m^3$
071978-1	1255	541
071978-2	1300	490
071978-5	1313	490
071978-6	1318	592
071978-12	1345	755
071978-13	1348	684
071978-14	1353	704
071978-17	1405	776
071978-24	1502	736
071978-26	1509	736
071978-31	1532	724
071978-32	1536	847
071978-34	1544	817

Average Values for 7/19/78		
	$\overline{X}$	684
	S_d	118
	C_v	0.17

TABLE 41. ANIMAL CHAMBER STUDIES - ALL QUANTITATIVE SAMPLES TAKEN BY ARC ON 7/20/78

ARC Sample No.	Time	$\mu g\ H_2SO_4/m^3$
072078-1	0925	735
072078-8	1004	613
072078-9	1008	664
072078-12	1033	511
072078-21	1258	642
072078-27	1341	551
072078-28	1344	756

Average value for 7/20/78		
	$\overline{X}$	639
	S_d	90
	C_v	0.14

TABLE 42. ANIMAL CHAMBER STUDIES - INDIVIDUAL SAMPLE COMPARISON BETWEEN EPA AND ARC SAMPLES

Date Sample Taken	Time of Sampling	Real Time Total Sulfur Chamber Concentration FPD (ppb)	ARC Sample No.	ug H_2SO_4/m^3 (ARC)	Equivalent EPA Sample No.	ug H_2SO_4/m^3 (EPA)
7/19	12:55-1:45 PM	111	071978-1	541	33-138	309
		109	071978-2	490	33-139	246
		111	071978-5	490		
		111	071978-6	592		
				$\bar{X}$ 528		$\bar{X}$ 278
				S_d 48		S_d 44
				C_v 0.09		C_v 0.16
7/19	2:37-3:27 PM	114	071978-24	736	33-140	599
		113	071978-26	736	33-141	499
				$\bar{X}$ 736		$\bar{X}$ 549
				S_d 0		S_d 71
				C_v 0		C_v 0.13
7/20	9:18-10:08 AM	105	072078-1	735	33-142	603
		106	072078-8	613	33-143	500
		106	072078-9	664		
				$\bar{X}$ 671		$\bar{X}$ 552
				S_d 62		S_d 73
				C_v 0.09		C_v 0.13
7/20	10:23-11:13 AM	105	072078-12	511	33-144	603
					33-145	510
				$\bar{X}$		$\bar{X}$ 556
				S_d -		S_d 66
				C_v -		C_v 0.12
7/20	1:26-2:16 PM	107	072078-27	551	33-146	281
		108	170278-28	756	33-147	241
				$\bar{X}$ 653		$\bar{X}$ 261
				S_d 144		S_d 28
				C_v 0.22		C_v 0.11
7/20	3:32-4:22 PM	114	Samples taken for thermal decomposition studies during this period.		33-148	597
					33-149	466
						$\bar{X}$ 531
						Sd 93
						C_v 0.18

TABLE 43. ANIMAL CHAMBER STUDIES - DAILY AVERAGE DATA SUMMARY COMPARISON BETWEEN EPA AND ARC SAMPLES

7/19/78		7/20/78	
ARC	EPA	ARC	EPA
541	309	735	603
490	246	613	500
490	599	664	603
592	499	511	510
736		551	281
736		756	241
			597
			466
$\overline{X}$ 598	$\overline{X}$ 413	$\overline{X}$ 638	$\overline{X}$ 475
S_d 114	S_d 164	S_d 98	S_d 142
C_v 0.19	C_v 0.40	C_v 0.15	C_v 0.30

TABLE 44. ANIMAL CHAMBER STUDIES - AVERAGED DATA (Questionable samples deleted)

	7/19/78		7/20/78	
	ARC	EPA	ARC	EPA
	$\mu g\ H_2SO_4/m^3$	$\mu g\ H_2SO_4/m^3$	$\mu g\ H_2SO_4/m^3$	$\mu g\ H_2SO_4/m^3$
$\overline{X}$	598	549	638	546
S_d	114	71	98	62
C_v	0.19	0.13	0.15	0.11

at the Junction of Route 55 and Rural Route 616 halfway between Strasburg and Front Royal, Virginia. The results of these experiments are shown in Table 45.

TABLE 45. RESULTS OF ENVIRONMENTAL FIELD TESTS - RURAL AREA (SAMPLE RATE 10 ℓ/MIN)

Sampling Time	ARC Sample No.	μg H_2SO_4/m^3	EPA Sample No.	H^+
10:00 AM - 1:00 PM	112278-1NMF	0	112278-1UF	Neutral
1:10 PM - 5:10 PM	112278-2NMF	0	112278-2UF	Neutral

Two sets of roadside samples were taken on a heavily traveled portion of Interstate 522 located within the Front Royal, Virginia, city limits. The sampling location was near the apex of a 60° hill within 15 feet of the roadside. A sulfuric acid production plant (H_2SO_4 aerosol), a power plant (SO_2), and a rayon production plant (H_2S, CS_2) were all located within a two mile radius of the sampling point. The results, which were expected to show ambient sulfate levels are given in Table 46.

TABLE 46. RESULTS OF ENVIRONMENTAL FIELD TESTS - URBAN AREA (SAMPLE RATE 10 ℓ/min)

Sampling Time	ARC Sample No.	μg H_2SO_4/m^3	EPA Sample No.	H^+
10:45 AM - 1:55 PM	112478-1NMF	6.0	112478-1UF	Basic
2:30 PM - 6:10 PM	112478-2NMF	9.6	112478-2UF	Basic

Samples collected simultaneously with the ARC samples shown in Tables 45 and 56, but not treated with fixing reagent, were sent to EPA contractor laboratories at Research Triangle Park for analysis for H^+, NH_4^+, and $SO_4^=$. Due to a misinterpretation, however, only H^+ was measured. The results of the H^+ analysis are included in Tables 45 and 46. No sulfuric acid was found in the rural area, which is confirmed by the EPA findings of a neutral H^+ concentration for the pertinent samples (Table 45). The urban area samples showed the presence of sulfates as expected, with the EPA H^+ readings of basicity for each sample indicating the possible formation of ammonium sulfate artifact during sample collection (Table 46). Basic species would not originally be anticipated in such close proximity to a roadside sampling network.

SUMMARY

Gas-phase fixation of sulfuric acid aerosol by a volatile amine or amine derivative was proposed as a convenient and effective method of stabilizing the acid aerosol prior to sample collection. In addition, it was suggested that the adduct could be conveniently analyzed if it decomposed to evolve SO_2 gas at a temperature below that of anticipated ambient particulate sulfates. In order to determine at which temperature the adducts could be selectively decomposed, various potentially interfering sulfates were taken from reagent bottles and subjected to Differential Thermal Analysis (DTA). All of the sulfates examined by DTA were found to decompose above 200°C. Thus, it was concluded that the ideal fixing reagent should react with H_2SO_4 aerosol to form an adduct which could be decomposed below 200°C and evolve SO_2 gas as a product.

The diethylamine (DEA), acetaldoxime (AAO) and diethylhydroxylamine (DEHA) derivatives of H_2SO_4 were subjected to DTA in order to determine the temperature at which they decomposed. It was established that each adduct decomposed at a temperature below the decomposition temperature of anticipated interferences. A flame photometric detector (FPD) was subsequently used to establish that volatile sulfur gases were evolved during decomposition. Sulfur dioxide was identified as a major product during the decomposition of each of the above adducts by mass spectrometry and West-Gaeke analyses. Infrared spectra were also obtained for the acetaldoxime and the diethylhydroxylamine adducts of sulfuric accid. A peak at 1650 cm^{-1} in the infrared spectra of both adducts indicated an N-H bending vibration which was attributed to protonation of nitrogen in the basic fixing reagent. It appeared that the basic fixing reagents reacted rapidly with sulfuric acid by proton transfer, forming a bisulfate salt. Rapid reaction kinetics is a desirable characteristic since the tendency for sulfuric acid to react with other species during the collection process would be lessened.

A Thomas aerosol generator, which reportedly supplies aerosol droplets in the 0.005 to 0.3 micrometer size range, was used to make sulfuric acid aerosol. The Thomas generator was used with each of the previously mentioned fixing reagents to produce a corresponding sulfuric acid adduct. This was accomplished by concurrently passing both fixing reagent and sulfuric acid aerosol through a reaction chamber connected between the Thomas generator and the sample collection filter. The Teflon filters containing the adduct were then placed in the Teflon decomposition chamber and heated to 200°C. It was established with this technique that the fixation process was very rapid and essentially complete after a few seconds. In addition, it was shown using the FPD that the sulfur gas evolved from the decomposition of the adducts was proportional to the quantity of sulfuric acid aerosol sampled.

Ammonium sulfate and ammonium bisulfate were considered to be a primary interference problem due to the close chemical similarity to H_2SO_4 and the relatively large amount of each species thought to be present in the environment. Differential Thermal Analysis of reagent grade ammonium sulfate and bisulfate indicated that both salts were stable to at least 250°C and 230°C, respectively. Experiments with the FPD indicated that no volatile sulfur species was evolved by either of these salts until at least 230°C. When ammonia was passed through a filter on which acid aerosol from the Thomas generator had been collected unfixed, as is normally the case in environmental sampling, no FPD signal was detected at 200°C. Thus, interference from this source was apparently not present for adducts prepared using acid aerosol particles in the 0.005 to 0.3 micrometer size range.

It was recognized that ambient sulfur gases such as SO_2, H_2S and COS might react with fixing reagents to form complexes which could be collected and subsequently decomposed along with the sulfuric acid adduct. Since the FPD responds to any sulfur species, the complexed sulfur gas could constitute a positive interference. To test this possibility, each of the above gases was mixed with DEA, DEHA and AAO fixing reagent and passed through Mitex LS filters for several minutes. The filters were then subjected to a rising temperature in the decomposition chamber to determine both the presence of a volatile sulfur species and the temperature at which it was produced. It was found that of the three sulfur gases, only SO_2 was significantly collected, and in every case, the SO_2-reagent complex had a very low thermal stability compared to that of the H_2SO_4 adduct. Thus, the interference could be eliminated by pre-heating the filter to an intermediate temperature where the SO_2-reagent complex would be removed before decomposition of the H_2SO_4 adduct at a higher temperature.

A Baird aerosol generator, which reportedly supplies aerosol particles in the 1 to 3 micrometer size range was also selected for this study because it was thought that the closed system design would give more reproducible aerosols than the Thomas generator. Initially, the adducts formed using the Baird generator were decomposed in order to verify decomposition temperatures. The results were surprising in that the adducts previously investigated using the Thomas generator now had decomposition temperatures that were different. The decomposition temperature (as determined by the evolution of sulfur gas) of the AAO and DEA adducts shifted upward while the DEHA adduct shifted downward. Of the three adducts, only that of AAO showed a substantial change. One possible explanation for the shift in adduct decomposition temperature was that the various aerosol generation methods which resulted in aerosol particles of widely different size range also resulted in particles with a large difference in free surface energy. This difference in free surface energy resulted in corresponding differences in individual adduct decomposition temperatures. However, it was observed that the most significant shift in decomposition temperature occured with the AAO adduct which contains an unsaturated bond. An additional study using n-methylformamide (NMF) which also has an unsaturated bond was also found to exhibit a very big difference in decomposition temperature. Thus, it appeared that the chemical nature of the fixing reagent in conjunction with the aerosol generation method affect the decomposition temperature of specific H_2SO_4 adducts. This may be due in part to the fact that the collection temperature of the Thomas generator aerosol was approximately 60° C. while the Baird generator aerosol was collected at approximately 30° C. The collection temperature difference was due to the flame generation method used in the Thomas generator.

The questions associated with the decomposition of the various adducts led to a reinvestigation of the major anticipated interferent, $(NH_4)_2SO_4$. The Baird generator was used to deposit $(NH_4)_2SO_4$ aerosols made from 0.01 N and 0.001 N $(NH_4)SO_4$ solutions. It was assumed that since less $(NH_4)_2SO_4$ per droplet would be present, this would result in a smaller particle when dry. The above solutions were also deposited on filters by pipet. In addition, $(NH_4)_2SO_4$ was formed using the H_2SO_4 aerosol obtained from the Thomas generator.

When the Baird aerosol generator was used to deposit samples from a solution of 0.01 N $(NH_4)_2SO_4$, an average value of 175° C. was found to be the initial temperature at which the aerosol decomposes. However, when the identical solution was deposited by pipet and subjected to the analysis procedures an average initial decomposition temperature of 183° C. was obtained. When the Baird generator was used to deposit the 0.001 N $(NH_4)_2SO_4$ solution, the initial response temperature dropped to an average of 165° C. Simultaneous exposure of H_2SO_4 aerosol produced by the Thomas generator to NH_3 resulted in a further decline of the observed initial decomposition temperature of $(NH_4)_2SO_4$ to an average of 158° C. However, when the H_2SO_4 aerosol was first collected and then exposed to NH_3 the initial $(NH_4)_2SO_4$ decomposition temperature rose to an average of 220° C. It is thought that the lack of agreement in the Thomas generator results is due to H_2SO_4 aerosol droplet growth on the collection surface prior to the addition of NH_3. Thus, it appears that particle size does influence the decomposition temperatures of the various species to a large degree. This is a particularly significant problem requiring further study since the distribution of sulfuric acid aerosols in the environment is thought to cover a large size range which indicates that the corresponding adducts would also deviate considerably.

Ambient ammonia, which was considered to be the primary negative interference due to reaction with sulfuric acid on collection surfaces, was investigated during this study. As originally conceived, a desirable aspect of the proposed method was the prediction that sulfuric acid adducts would be less likely to react during the collection process than the original acid aerosol. The relative reactivity between ammonia, H_2SO_4 aerosol and various H_2SO_4 adducts was therefore determined. It was found that the reaction between ammonia and sulfuric acid was suppressed on collection surfaces as the result of forming sulfuric acid adducts during the collection process.

The success of the proposed research approach also depends upon whether a reproducible stoichiometric relationship exists between the sulfur gases evolved during adduct decomposition and the H_2SO_4 originally present in the sample stream. It was originally hypothesized that the gases evolved during adduct decomposition should consist primarily of SO_2. Therefore, experiments were performed to obtain information about the reproducibility of the Baird generator and the quantity of SO_2 evolved at 200° C. from the AAO adduct. The West-Gaeke technique was used instead of the FPD to measure the evolved gases since it was reportedly specific for SO_2. It was found that the amount of H_2SO_4 aerosol collected during identical runs was reproducible to within $\pm 10\%$ based upon the amount of SO_2 evolved during the thermal decomposition process. Thus, it appears that the Baird generator is fairly reproducible, as is the evolution of SO_2 from an identical quantity of AAO adduct. Additional tests using three different volumes of the identical H_2SO_4 aerosol stream were sampled in the ratio of 1:2:3. The corresponding H_2SO_4 adducts when decomposed were found to evolve SO_2 gas in approximately the identical ratio. Thus, it appears that AAO can be used to fix H_2SO_4 aerosol in a moving gas stream to form an adduct which can be decomposed to give off an amount of SO_2 that is related to the volume of aerosol stream sampled.

In order to determine an exact stoichiometric relationship between the SO_2 evolved during adduct decomposition and the original H_2SO_4 aerosol present, known amounts of H_2SO_4 were deposited on Mitex filters by pipet. An equal volume of fixing reagent was then applied to the sample and dried. Decomposition of the adducts at 200° C. showed that the stoichiometric relationship between the SO_2 evolved and the original acid aerosol was reproducibly one mole of SO_2 to three moles of H_2SO_4 when both the sampling and analysis were accomplished under controlled laboratory conditions. Experiments identical to those above for the AAO adduct were also performed for DEHA and DEA derivatives of sulfuric acid. It was found that the DEHA adduct evolved SO_2 in a ratio of one mole of SO_2 to two moles H_2SO_4 and the DEA adduct evolved SO_2 in a stoichiometric ratio of one mole of SO_2 to one mole of H_2SO_4.

The AAO, NH_3 and NMF adducts of sulfuric acid were found to give off gaseous sulfur species in a stoichiometric ratio of one mole of SO_2 to three moles of sulfuric acid during thermal decomposition. Using the above values, a mass balance was made between measured H_2SO_4 aerosol concentration and the predicted aerosol concentration based on the generator's operating conditions. Calculations predicted that the H_2SO_4 aerosol concentration should be 123 $\mu g/m^3$ while measurements using a fixing reagent coupled with thermal decomposition found the concentration to be 111 $\mu g/m^3$. In addition, field tests using the Environmental Protection Agency's Animal Test Chambers at Research Triangle Park resulted in close agreement between the amount found by the gas phase fixation methodology and the Thorin technique used by the EPA.

The alternate approach of eliminating sulfate particulate interference by selectively volatilizing sulfuric acid and passing it through a prefilter was investigated during this study. It was found that at temperatures up to 200°C, sulfuric acid aerosol in the low μg range could not be volatilized and efficiently passed through a prefilter.

In conclusion, it appears that the gas-phase fixation of sulfuric acid aerosol by a volatile amine or amine derivative offers definite advantages over existing techniques. Among these are ease of calibration using SO_2 standards rather than H_2SO_4, increased sensitivity and suppression of side reactions. However, the apparent effect of particle size on decomposition temperature must be resolved before the method can be used to satisfactorily eliminate ammonium sulfate interferences.

REFERENCES

1. Firket, J., "Fog Along the Meuse Valley," *Trans. Faraday Soc.*, Vol. 32, 1102 (1936).

2. Schrank, H., H. Heimann, G. Clayton, W. Gafaffer and H. Wexler, "Air Pollution in Donora, Pa.," Public Health Bulletin, Washington, No. 306 (1949).

3. Stern, A. C., ed., "Air Pollution and Its Effects" in *Air Pollution: A Comprehensive Treatise*, Vol. 1, Academic Press, New York (1968).

4. Leighton, P., "Photochemical Secondary Reactions in Urban Air" in *Photochemistry of Air Pollution*, Pergamon Press, London (1957).

5. Pemberton, J. and C. Goldberg, "Air Pollution and Bronchitis," *Brit. Med. J.*, *567*, Sept. 4 (1954).

6. Amdur, M., "Toxicologic Appraisal of Particulate Matter, Oxides of Sulfur and Sulfuric Acid," *J. Air Pollut. Contr. Ass.*, *19*, 683 (1969).

7. Amdur, M., R. Schulz and P. Drinker, "Toxicity of Sulfuric Acid Mist to Guinea Pigs," *Arch. Ind. Hyg. Occup. Med.*, *5*, 318 (1952).

8. Leithe, W., *The Analysis of Organic Pollutants in Water and Waste Water*, Ann Arbor, Ann Arbor, Mich., 13 (1973).

9. Koide, M. and E. Goldberg, "Atmospheric Sulfur and Fossil Fuel Combustion," *J. Geophys. Res.*, *76*, 6589 (1971).

10. Wolf, P., "Carbon Monoxide, Measurement and Monitoring in Urban Air," *Environ. Sci. and Tech.*, *5*, 212 (1971).

11. McEwen, D., "Automobile Exhaust Hydrocarbon Analysis by Gas Chromatography," *Anal. Chem.*, *38*, 1047 (1966).

12. Stephens, E. and M. Price, *Aerosols and Atmospheric Chemistry*, ed. by G. Hidy, Academic Press, New York, 167 (1972).

13. Raymond, A. and G. Guiochon, "Gas Chromatographic Analysis of C_8-C_{18} Hydrocarbons in Paris Air," *Environ. Sci. and Tech.*, *8*, 143 (1974).

14. Pellizzari, E., J. Bunch, E. Berkley and J. McRae, "Determination of Trace Hazardous Organic Vapor Pollutants in Ambient Atmospheres by Gas Chromatography/Mass Spectrometry/Computer," *Anal. Chem.*, *48*, 803 (1976).

15. Habibi, K., "Characterization of Particulate Matter in Vehicle Exhaust," Environ. Sci. and Tech., 7, 223 (1973).

16. Blosser, E. R., "A Study of the Nature of the Chemical Characteristics Of Particulates Collected from Ambient Air," NTIS No. PB-220-401.

17. Urone, P. and W. Schroeder, "SO_2 in the Atmosphere: A Wealth of Monitoring Data, but Few Reaction Rate Studies," Environ. Sci. and Tech., 2, 8 (1968).

18. Sidebottom, H. and J. Calvert, "Photooxidation of Sulfur Dioxide," Environ. Sci. and Tech., 6, 1 (1972).

19. Friend, J., R. Leifer and M. Trichon, "On the Formation of Stratospheric Aerosols," J. Atmos. Sci., 30, 465 (1973).

20. Freiberg, J., "Effects of Relative Humidity and Temperature on Iron-Catalyzed Oxidation of SO_2 in Atmospheric Aerosols," Environ. Sci. and Tech., 8, 731 (1974).

21. Novakov, T., A. Harker and W. Siekhaus, "Sulfates as Pollution Particulates: Catalytic Formation on Carbon (soot) Particles," Science, 186 (1974).

22. Forester, P., "Oxidation of Sulphur Dioxide in Power Station Plumes," Atmos. Environ., 3, 157 (1968).

23. Katz, M., "Photoelectric Determination of Atmospheric Sulfur Dioxide," Anal. Chem., 22, 1040 (1950).

24. Scaringelli, R. P. and K. A. Rehme, "Determination of Atmospheric Concentrations of Sulfuric Acid Aerosol by Spectrometry, Coulemetry and Flame Photometry," Anal. Chem., 41, 707 (1969).

25. Takahashi, K., M. Kasahara and J. Katz, "A Kinetic Model of Sulfuric Acid Aerosol Formation from Photochemical Oxidation of Sulfur Dioxide Vapor," Aerosol Science, 6, 75 (1975).

26. Mirabel, P. and J. Katz, "Binary Homogeneous Nucleation as a Mechanism for the Formation of Aerosols, Journal of Chemical Physics, 60 (3), 1138 (1974).

27. Whitby, K., "Sulfuric Acid Review Conference," Hendersonville, N. C., Jan. 31, 1977 to February 3, 1977.

28. Amdur, M. O., "Aerosols Formed by Oxidation of Sulfur Dioxide: Review of Their Toxicology," Arch. Envir. Health, 23, 459 (1971).

29. Vanderpol, A., F. Carsey, D. Covert, R. Charlson and A. Waggoner, "Aerosol Chemical Parameters and Air Mass Character in the St. Louis Region," Science, 190, 570 (1975).

30. Willard, Richard L., Preprint, National Meeting Division Water, Air and Waste Chemistry, Am. Chem. Soc. (1973).

31. Meserole, F. B., *et al*., "Sulfur Dioxide Interferences in the Measurement of Ambient Particulate Sulfates," NTIS No. PB-249-620 (1976).

32. Faith, W. L., *Air Pollution Control*, John Wiley and Sons, Inc., New York, 143 (1959).

33. Taarit, Y. and J. Lunsford, "Electron Paramagnetic Resonance Evidence for the Formation of SO_3^- by the Oxidation of SO_2^- on MgO," *Journal of Physical Chemistry*, *11*, 1365 (1973).

34. Vohia, K. and P. Nair, "Chemical Formation of Aerosols in the Air by Gas Phase Reactions," *J. Aerosol Sci*., *1*, 127 (1970).

35. Kiang, C. and P. Hamill, "Sulfuric Acid-Nitric Acid-Water Ternary System in the Stratosphere," *Nature* (London), *250*, 401 (1974).

36. Lee, R. E. and J. Wagmen, "Sampling Anomaly in the Determination of Atmospheric Sulfate Concentration," *Amer. Ind. Hyg. Assn. J*., *27*, (3), 266 (1966).

37. Dubois, L., T. Teichman, R. S. Thomas and J. L. Monkman, Symposium on the Physico-Chemical Transformation of Sulfur Compounds in the Atmosphere and the Formation of Acid Smogs, Paris, December 1967, Paper No. 8.

38. Barton, S. C. and H. G. McAdie, "Preparation of Glass Fiber Filters for Sulfuric Acid Aerosol Collection," *Environ. Sci. and Technol*., *4*, 769, (1970).

39. Maddalone, R. F., A. D. Shendrikar and P. W. West, "Radiochemical Evaluation of the Separation of H_2SO_4 Aerosol by Microdiffusion from Various Filter Media," *Microchem. Acta*, *3* (1974).

40. Thomas, R. L., V. Dharmarajan and P. W. West, "Convenient Method for Generation of Sulfuric Acid Aerosol," *Environ. Sci. and Technol*., *8*, 930 (1974).

41. Maddalone, R. F., R. L. Thomas and P. W. West, "Measurement of Sulfuric Acid Aerosol and Total Sulfate Content of Ambient Air," *Environ. Sci. and Technol*., *10*, 162 (1976).

42. Thomas, R. L., V. Dharmarajan, G. L. Lundquist and P. W. West, "Measurement of Sulfuric Acid Aerosol, Sulfur Trioxide and the Total Sulfate Content of the Ambient Air," *Anal. Chem*., *48*, 639 (1976).

43. Liu, B. and K. Lee, "Efficiency of Membrane and Nucleopore Filters for Submicron Aerosols," *Environ. Sci. and Technol*., *10*, 345 (1976).

44. Kerrigan, J. V., K. Snajberk and E. S. Andersen, "Collection of Sulfuric Acid Mist in the Presence of a Higher Sulfur Dioxide Background," *Anal. Chem.*, 32, 1168 (1960).

45. Rastogi, R. and K. Kishore, "Kinetics and Mechanism of Reaction Between Alcohol and Sulfuric Acid at High Temperatures," *Ind. J. Chem.*, 7, 480 (1969).

46. dos Santos, Serpa, "Spectrophotometric Determination of Tetracycline by its Reaction with Concentrated Sulfuric Acid," *Bol. Fac. Farm., Univ. Coimbra, Ed. Cient.*, 31, 29 (1972).

47. Svirevski, I. and M. Miloshev, "Color Reaction Between Substituted Indenones and Concentrated Sulfuric Acid," *Dokl. Bolg. Okad. Nauk.*, 27 (3), 361 (1974).

48. Ladler, K., *Reaction Kinetics: Vol. II - Reactions in Solutions*, The Macmillan Company, New York, 85 (1963).

49. Huygen, C., "Simple Photometric Determination of Sulfuric Acid Aerosol," *Atmospheric Environment*, 9, 315 (1975).

50. Moeller, T., *Inorganic Chemistry*, 8th Printing, John Wiley (1959).

51. Weast, R. C., ed., *Handbook of Chemistry and Physics*, 49th ed., The Chemical Rubber Co., Cleveland, Ohio (1968).

52. Lange, N., ed., *Handbook of Chemistry*, 10th ed., McGraw-Hill Book Co., New York (1952).

53. Belcher, R., M. Kapel and A. Nutten, "Some Factors Influencing the Solubilities of Amine Sulfates," *Anal. Chim. Acta*, 8, 122(1953).

54. Belcher, R., A. Nutten and W. Stephen, "Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. XII. Reagents for the Precipitation of Sulfate," *J. Chem. Soc.*, 1334 (1953).

55. Stephen, W., "New Reagent for the Detection and Determination of Small Amounts of the Sulfate Ion," *Anal. Chim. Acta*, 50, 413 (1970).

56. Maddalone, R. F., G. L. McClure and P. W. West, "Determination of Sulfate by Thermal Reduction of Perimidylammonium Sulfate," *Anal. Chem.*, 47, 316 (1975).

57. Barrett, W., H. Miller, J. Smith, Jr. and C. Gwin, "Development of a Portable Device to Collect Sulfuric Acid Aerosol - Interim Report," Contractor Report EPA-600/2-77-027, Environmental Protection Agency, Research Triangle Park, N. C. (1977).

58. Raabe, O. G., *Fine Particles: Aerosol Generation Measurement, Sampling and Analysis*, ed. by B. Y. H. Liu, Academic Press, 57-110 (1976).

59. West, P. and G. Gaeke, "Fixation of Sulfur Dioxide as Disulfitomercurate(II) and Subsequent Colorimetric Estimation," Anal. Chem., 12, 1816 (1956).

60. Dubois, L., C. Baker, T. Teichman, A. Zdrojewski and J. Monkman, "Determination of Sulfuric Acid in Air," Mikrochimica Acta (Wien), 269, 1969.

61. Erdey, L., S. Gal and G. Liptay, "Thermoanalytical Properties of Analytical Grade Reagents: Ammonium Salts," Talanta, 11, 913 (1964).

62. Grundnes, J., S. Christian, C. Venghuot and S. Farnham, "Solvent Effects on Strong Charge-Transfer Complexes. IV. Trimethylamine and Sulfur Dioxide in the Vapor Phase," J. of the Am. Chem. Soc., 93, 20 (1971).

63. Landreth, R., R. de Pena and J. Heicklen, "Thermodynamics of the Reaction of Ammonia and Sulfur Dioxide in the Presence of Water Vapor," J. of Phys. Chem., 17, 1785 (1975).

APPENDIX A

REACTIONS IN FLOW SYSTEMS

REACTIONS IN FLOW SYSTEMS

It was necessary that the gas phase fixation concept and the reaction chamber design be evaluated analytically to insure that the total concept is theoretically feasible. In order to make a theoretical assessment of the system, approximate values were obtained for reagent concentrations, molecular collision frequencies, gas/liquid diffusion rates, reaction stoichiometry and reaction chamber residence time. Once these values were obtained, it was determined that the physical characteristics of the dynamic flow system were sufficiently rapid to allow complete fixation to occur during reaction chamber residence time.

The theoretical assessment of the proposed gas/liquid phase concept is the subject of this Appendix. A model is assumed for the fixation process and the separate elements of that model are examined analytically herein. The model can be described as follows: A mixture of gaseous fixing reagent at a given concentration in air enters into and mixes with the main flow stream of the apparatus, the latter consisting of micron-size droplets of sulfuric acid in air. Molecules of vapor fixing reagent (i.e., diethylamine) impinge upon the aerosol droplets, are absorbed at the surface, diffuse throughout each droplet, and react with the H_2SO_4. The time required for these events to occur is taken as the reactor residence time for the purposes of this analysis. The much longer time period, during which acid and reagent remain in contact on the filter is neglected. The preliminary design of a physical model which provides the necessary mixing and reaction zone is shown in Figure 1. The sample containing the acid aerosol (symbolized by "O" on the figure) would be drawn into the device at A, while the gaseous fixing reagent ("X") would then react in Zone C to form the adduct (OX) which would be collected on the filter medium. Residual gaseous fixing reagent would pass through the filter to the pumping source.

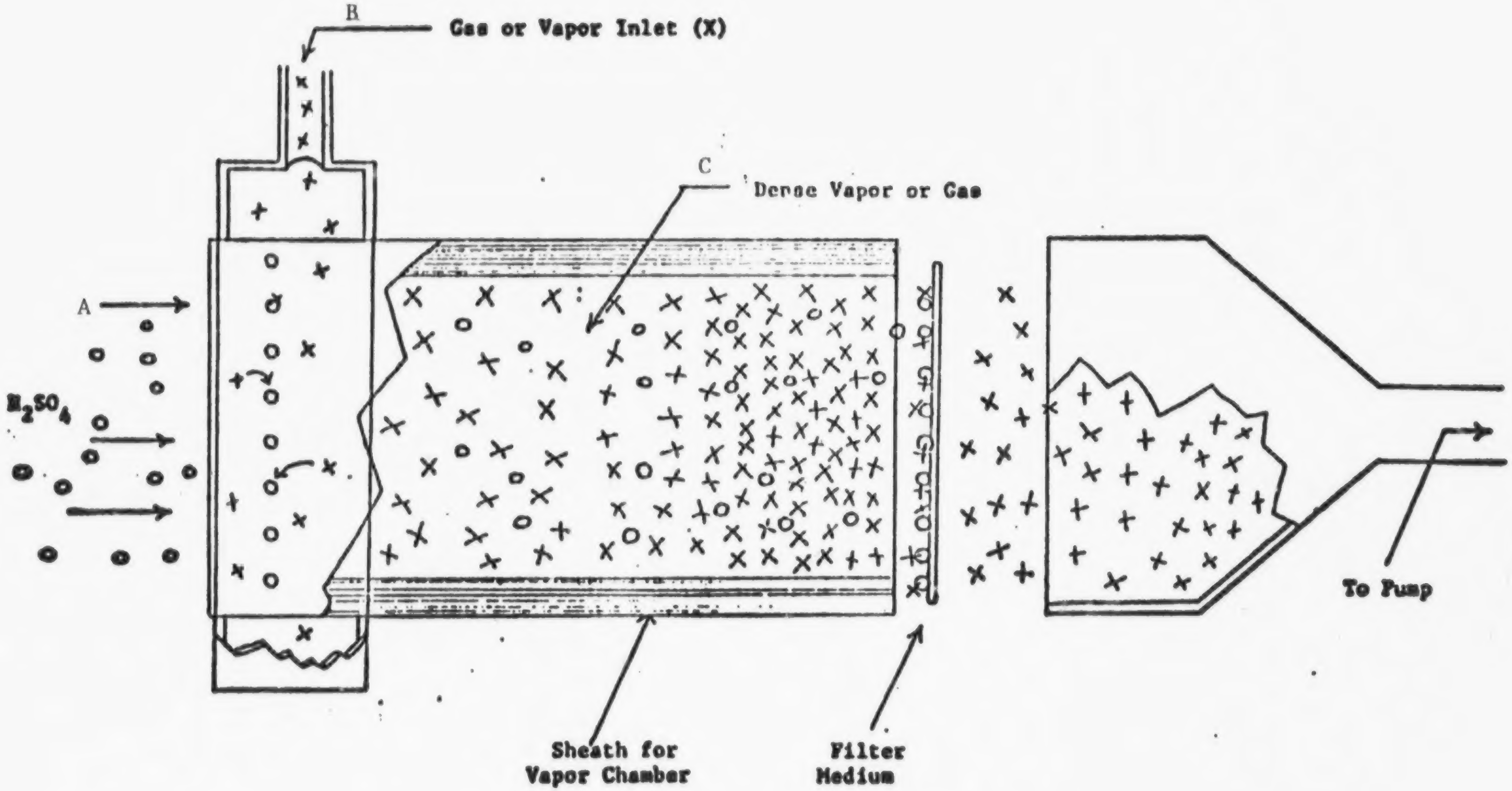

B
Gas or Vapor Inlet (X)
C
Dense Vapor or Gas
A
H_2SO_4
To Pump
Sheath for Vapor Chamber
Filter Medium

Figure 1. H_2SO_4 filter collection system (gas or vapor reagent).

DISCUSSION

A. Calculation of Reagent Vapor Concentration in the Vicinity of H_2SO_4 Collection Filters

Initially, to approximate the kinetics of the proposed method, the concentration of the various reagents in the reaction chamber must be considered. The reagents currently of interest in this study are diethylamine (DEA), diethylhydroxylamine (DEHA), acetaldoxime (AAO), dimethylamine (DMA) and hydroxylamine (HA). The vapor pressure at room temperature for each of the reagents above can be approximated from their known boiling points.

1. Vapor Pressure of Reagents

The boiling point is the temperature at which the vapor pressure equals atmospheric pressure. The use of Trouton's Rule:

$$\Delta\bar{S}_{vap} = \frac{\Delta H_{vap}}{T_{bp}} \cong 21 \text{ cal/°K mole} \qquad (1)$$

where ΔH_{vap} is in cal/mole and T_{bp} is the boiling point in °K, enables one to estimate the vapor pressure of non-polar liquids at a given temperature when the standard boiling temperature is known. Trouton's rule states that the molal entropy of vaporization ($\Delta\bar{S}_{vap}$) at the standard boiling point (T_{bp}) of many liquids is equal to approximately 21 cal/°K mole (1). While the proposed fixing reagents are not non-polar, Trouton's Rule may hold well enough to permit the estimation of reagent vapor pressures at room temperature.

In order to compute the vapor pressure of a liquid from its known boiling point, the Clausius-Clapeyron equation is used:

$$\log\frac{P_2}{P_1} = \frac{\Delta H_{vap}(T_2 - T_1)}{2.303\ RT_2T_1} \qquad (2)$$

where P_2 is atmospheric pressure when T_2 refers to the boiling point, and P_1 is the vapor pressure of the liquid at T_1.

Substituting (21 x T_b) for ΔH_{vap} from equation (1), converting to exponential form, and simplifying, equation (2) becomes:

$$P_1 = P_2 \exp\left[\frac{21(T_1 - T_2)}{RT_1}\right] \qquad (3)$$

The value of the gas constant R is 1.987 cal/mole degree.

Using the known boiling point value (T_2) for each reagent and taking T, as 298°K, approximate vapor pressures were computed at ambient temperature from equation (3). The results are collected in Table 1. Published values for the vapor pressure of diethylamine and acetaldoxime are 260 mm and 10 mm respectively (2). These values are in fairly good agreement with the calculated values in Table 1.

TABLE 1. Calculated Vapor Pressures

Reagent	Known B.P. (°C)	V.P. Calculated (25°C)
Diethylamine	55	262.3 mm
Dimethylamine	7.4	1418.5 mm
Acetaldoxime	114	32.3 mm
Hydroxylamine	110	37.3 mm
Diethylhydroxylamine	125	21.9 mm

2. Concentration of Vapors

The reagent vapors which enter B of Figure 1 are produced by bubbling air through the volatile reagents. This saturated or partially saturated gas stream is further diluted by the sample air stream entering at point A of Figure 1. The concentration of each reagent vapor in the gas stream at B is simply the ratio of each reagent's vapor pressure (Table 1) to the total pressure of the systems. Thus, if it is assumed that the dynamic gas stream is saturated with vapor and that it is at atmospheric pressure, the concentration becomes:

$$C_b = \frac{VP_{C_b}}{760} \times 100 \qquad (4)$$

where C_b is the reagent vapor concentration in terms of volume percent. By using the vapor pressure values of Table 1 with equation (4), the values shown in Table 2 are computed as the approximate concentrations of the various fixing agents at point B of the H_2SO_4 collection system.

The flow of the gas stream entering the reaction chamber at B is estimated to be 0.5 l/min, while the sample stream has a maximum flow of approximately 34 l/min. Thus, the concentration of vapors in the reaction zone is:

$$C_c = \frac{0.5}{34} \times C_b \qquad (5)$$

where C_b and C_c represent the volume percent reagent concentration at points B and C respectively. The values for the concentrations at C are given in Table 3.

B. Rate of Reaction of Fixing Reagents with H_2SO_4 Aerosol

Once the concentration of vapors in the reaction manifold has been defined, estimates can be made to determine if the rate of various processes are sufficiently rapid to permit complete reaction during the time the sample and vapors transverse the reaction chamber (C).

1. Molecular Collisions

Since the proposed method involves the reaction of a vapor with an aerosol particle (liquid surface), the calculation of the number of collisions per second per unit area would serve as an indication of the rate of reagent impingement that could be anticipated on the surface of the aerosol droplet. The rate of molecular collisions per unit area is given as:

Table 2. Estimated Vapor Concentration at Inlet (Section B of Figure 1)

Reagent	Volume %	ppm
Diethylamine	34	3.4×10^5
*Dimethylamine	100	1.0×10^6
Acetaldoxime	4.2	4.2×10^4
Hydroxylamine	4.9	4.9×10^4
Diethylhydroxylamine	2.9	2.9×10^4

*Dimethylamine boils at 7.4°C and has a calculated vapor pressure of 1418 mm at 25°C. Thus, dimethylamine does not require a diluent carrier, and enters as a pure vapor at point B in the collection system.

TABLE 3. Estimated Vapor Concentration in Manifold (Section C of Figure 1)

Reagent	Volume %	ppm
Diethylamine	0.50	5,000
Dimethylamine	1.5	15,000
Acetaldoxime	0.06	600
Hydroxylamine	0.07	700
Diethylhydroxylamine	0.04	400

$$\frac{\text{Collisions}}{\text{cm}^2\text{sec}} = 0.230\text{ nu} \qquad (6)$$

where 0.230 is the directional characteristic for molecules striking a given surface, assuming that the molecules travel in a random direction. The number of reagent molecules per cubic centimeter is represented by n in equation (6) and denotes the concentration of the vapor in the reaction zone (C) of Figure 1. The approximate concentrations of the various reagents in the reaction zone are given in Table 3. The term u in equation (6) is the average root mean square velocity of ideal gaseous molecules in motion and is equal to:

$$u = \frac{\sqrt{3RT}}{m} \qquad (7)$$

where T is temperature (298°K), m is molecular weight of each reagent, and R is the gas constant (8.314×10^7 joules degree^{-1} mole^{-1}). Combining equation (6) with equation (7) gives

$$\frac{\text{Collisions}}{\text{cm}^2\text{sec}} = 0.230\ n\frac{\sqrt{3RT}}{m} \qquad (8)$$

Collisions/cm^2 sec, calculated using equation 8, are given in Table 4 for each of the candidate reagents. As can be seen from the table, on the order of 10^{20} collisions/cm^2sec can be anticipated based upon estimates of reagent concentration within the reaction chamber.

2. Residence Time in Reaction Manifold

The amount of time available for the reaction to occur is determined by the volumetric flow rate of the gas and the length and cross sectional area of the reaction tube. The diameter of the tube is 2.5 cm and its length is 20 cm, which yield a volume of 98 cm^3.

Since the flow through the reaction chamber is known to be 34 l/min or 0.57 l/sec, the residence time in the reaction chamber (c) is:

TABLE 4. Collisions/cm^{2}sec at 298°K
for Candidate Reagents

Reagent	m	n* molecules/cm^3	u (cm/sec)	Collisions cm^{2}sec
Diethylamine	73	1.1×10^{17}	3.2×10^{4}	8.1×10^{20}
Dimethylamine	45	4.0×10^{17}	4.1×10^{4}	3.7×10^{21}
Acetaldoxime	59	1.6×10^{16}	3.5×10^{4}	1.3×10^{20}
Hydroxylamine	33	2.0×10^{16}	4.7×10^{4}	2.2×10^{20}
Diethylhydoxylamine	89	1.2×10^{16}	2.9×10^{4}	7.8×10^{19}

*Based upon vapor concentrations in Table 3.

$$\frac{0.098\ 1}{0.571/\text{sec}} = 0.17 \text{ seconds or} \approx 200 \text{ milliseconds.}$$

3. Vapor/Aerosol Collisions During Chamber Residence

The aerosol droplets are estimated to be of the order of one micron in diameter. The surface area of a sphere is

$$S_A = \pi D^2 \tag{9}$$

where D is the sphere diameter. Therefore, the surface area of a one micron sphere is $3.14 \times 10^{-8}\text{cm}^2$.

The number of collisions/cm^{2}sec for each of the candidate reagents were previously calculated and are given in Table 4. Thus, since the surface area of an aerosol droplet one micron in diameter is known, and the molecular collision rate for each reagent has been estimated, then the total number of collisions of reagent vapor with an aerosol droplet is:

$$\text{Total collisions} = \frac{\text{collisions}}{\text{cm}^2\text{ sec}} \times 3.14 \times 10^{-8}\text{cm}^2 \times 0.2 \text{ sec} \tag{10}$$

for the measured residence time in the reaction chamber. Total collisions for each of the reagents with an aerosol droplet as it passes through the reaction chamber are given in Table 5.

TABLE 5. Total Reagent Vapor/Aerosol Collisions During Reactor Residence

Reagent	Total Collisions
Diethylamine	5.1×10^{12}
Dimethylamine	2.3×10^{13}
Acetaldoxime	8.2×10^{11}
Hydroxylamine	1.4×10^{12}
Diethylhydroxylamine	4.9×10^{11}

4. Molecules H_2SO_4 in One Micron Aerosol Droplet

The stoichiometric reaction of reagent vapors with H_2SO_4 molecules in an aerosol droplet requires that a sufficient number of reagent molecules impinge on a droplet during reaction chamber residence time to completely react with the H_2SO_4 molecules. An assessment of this criteria requires that a correlation be made between the total molecular collisions from the vapor and the actual H_2SO_4 molecules within the aerosol droplet.

The number of molecules of H_2SO_4 within an aerosol droplet of known molarity is:

$$\frac{\text{molecules } H_2SO_4}{\text{droplet}} = V_D \times C_M \times 6 \times 10^{23} \qquad (11)$$

where V_D is the aerosol droplet volume, C_M is the molar concentration of H_2SO_4 and 6×10^{23} is the number of molecules per mole. Current estimates for the concentration of H_2SO_4 in ambient aerosols range from approximately 0.01 to 7.0 molar, depending upon the relative humidity and the aerosol particle size. Taking the worst theoretical case, 7.0 molar H_2SO_4 aerosol and a one micron droplet size, the number of molecules of H_2SO_4/one micron droplet becomes:

$$\frac{\text{Molecules } H_2SO_4}{1\mu \text{ droplet}} = 1/6\pi(10^{-4}\text{cm})^3 \times 7 \text{ moles}/\ell \times \frac{1\ell}{1000\text{cc}} \times$$

$$6 \times 10^{23} = \approx 2 \times 10^9 \text{ molecules } H_2SO_4/\ 1\mu \text{ droplet}$$

Based upon a comparison of values from Table 5 of total collisions ($\approx 10^{12}$) with total H_2SO_4 molecules within an aerosol droplet ($\approx 10^9$), it can be concluded that sufficient collisions occur to completely react all H_2SO_4. Thus, the rate of collisions of reagent molecules with the aerosol droplets is not a controlling factor, if the "sticking coefficient" is $10^9/10^{12}$ or greater than 10^{-3}. The term "sticking coefficient" refers to the molecular collisions that stick to or penetrate the aerosol droplet rather than bounce or ricochet off the surface. The reagents proposed for this program may have "sticking coefficients" near unity, since they are highly water soluble.

5. Characteristic Molecular Diffusion Time in a Liquid

The reaction between vapor molecules and H_2SO_4 molecules is most likely to take place throughout the aerosol droplet. There are several reasons for this: first, the H_2SO_4 is distributed throughout the droplet; secondly, the reagents are soluble in H_2O; and finally, the H_2SO_4 adducts are also water soluble. Thus, an important criteron is the rate at which the molecular species distribute themselves throughout the aerosol droplet, since this will also determine the reaction rate.

The diffusion of molecular species can be estimated using:

$$X^2 = 2Dt \tag{12}$$

where X is a mean diffusion distance, D is the diffusion coefficient and t is a characteristic diffusion time. Using the one micron aerosol dimension for X and a value of $10^{-5}\text{cm}^2/\text{sec}$ for D* in equation (12), t is estimated to be 5×10^{-4}sec or ≈ 1 millisecond.

---

* $10^{-5}\text{cm}^2/\text{sec}$ is a typical value for the diffusion of molecular species in liquids (Chemical Rubber Handbook, 56th edition, page F-60).

Since the reactor residence time is approximately 200 milliseconds and the diffusion time for molecular species in a one micron droplet is of the order of one millisecond, there is sufficient time for diffusional mixing throughout the aerosol droplet.

6. Conclusions

There are many physical processes involved in the fixation of H_2SO_4 molecules within an aerosol droplet. The calculations, based upon the experimental model show that reagent concentrations in the reaction zone are adequate to generate sufficient molecular collisions to completely fix the H_2SO_4 during reaction chamber residence. In addition, diffusion of reagent vapors in the aerosol droplet is sufficiently fast to permit fixation of the H_2SO_4 throughout the droplet's volume during reaction chamber residence. Thus, the theoretical examination of the physical processes involved during gas phase fixation of H_2SO_4 aerosol indicates that it is a feasible approach. This, of course, assumes that the chemical reaction between H_2SO_4 and the basic amines occurs at a high rate relative to physical processes.

REFERENCES CITED

1. Daniels, F. and R. Alberty, Physical Chemistry, 3rd ed., p. 159, John Wiley, 1966.

2. Weast, R., ED., Handbook of Chemistry and Physics, 56th ed., The Chemical Rubber Company, Cleveland, OH (1975).

APPENDIX B

MEASUREMENT TECHNIQUES FOR SULFURIC ACID AND SULFURIC ACID ADDUCTS

MEASUREMENT TECHNIQUES FOR SULFURIC ACID AND SULFURIC ACID ADDUCTS

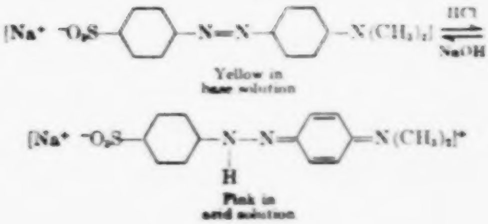
Sulfuric acid undergoes reaction with many types of compounds that could conceivably yield a sulfuric acid adduct worthy of investigation. The sulfuric acid adducts will be of varying physical and chemical descriptions and each will probably require a unique analytical approach in order to evaluate its merit. The adducts must be examined for stability, stoichiometry, speed of formation and interference effects. Clearly, the analysis of each adduct can be a considerable effort, since the concentrations will be low and the physical states varied. Various analytical methods and their potential for measurement of sulfuric acid and sulfuric acid adducts are discussed below.

Wet Chemistry Techniques

The sulfuric acid molecule consists of two species, H^+ and SO_4^{-2}, which can be used to measure its concentration. The measurement of either species is not specific for sulfuric acid when other acids or sulfates are present. Once the sample is dissolved, interfering species contributing H^+ or SO_4^{-2} ions cannot be distinguished from the ions generated by sulfuric acid. Thus, the applicability of wet chemical techniques to the analysis of sulfuric acid necessitates a viable separation technique that eliminates potential interferences before dissolution.

1. Proton Measurement

Many investigators have used proton measurement techniques to determine sulfuric acid content. Most of these indicators are organic dyes which exist in two forms: the base form possesses one color which by gain of a proton is converted to a different colored acid form. An example of this mechanism, the reaction of methyl orange with one proton, is given below.



Assume that a sample of sulfuric acid was collected on a fiberglass filter. The filter could then be sprayed from an aerosol can with a selected indicator. The indicator could be dissolved in an organic solvent to prevent possible hydrolysis of metal sulfates forming colored products. The intensity of this color would serve as a preliminary indication of the amount of sulfuric acid present, determining whether laboratory analysis is necessary. This further analysis can be performed by dissolving the dye in a non-colored, non-chromophoric organic solvent, and determining the concentration spectrophotometrically.

Some indicators that have been used to determine H_2SO_4 aerosol include methyl red, neutral red, methyl orange, bromocresol green, methylthymol(1), and bromophenol blue (2).

The acid-base indicator method would be subject to interference from other non-volatile acids, such as H_3PO_4, but volatile acids such as HCl would not be retained by the filter during collection. The indicator spray, however, must not be added prior to sampling, because the volatile acids would react as they passed through the filter. In addition, metal sulfates should not interfere to a significant degree, as the color formed is due to the protons of the sulfuric acid. Since the reaction is run in organic solvents, no dissolution of these sulfates should occur. This technique should work on any of the collection techniques previously described, where the volatile acids are not collected with sulfuric acid.

2. Classical Techniques for Sulfate Analysis

The classical methods of sulfate analysis could be applied to the problem of measuring sulfuric acid, if interfering sulfates were eliminated during sample collection, or if the preferential release of sulfuric acid were realized. Essentially, this would be total sulfate analysis with other sulfates being absent. The main thrust of the newer literature on sulfate analysis has been aimed at modification of four main procedures: 1) gravimetry, 2) titrimetry, 3) colorimetry, 4) turbidimetry or nephelometry. This has been done in order to achieve greater accuracy and to eliminate interferences.

a. Gravimetry

The classical, though seldom used, method for analysis of sulfate is by precipitation of barium sulfate from a hot, slightly acid solution by the addition of barium chloride:

$$SO_4^{=} + Ba^{++} \rightarrow BaSO_4\downarrow$$

The precipitate must be digested, filtered, the paper ignited, and the residue weighed as $BaSO_4$. The procedure is long and tedious, and subject to many interferences due to coprecipitation of other substances. Interfering substances are largely cations such as lead, strontium, and calcium which form insoluble sulfates, although anions of weak acids, nitrates, chlorates and heavy metal ions interfere if care is not taken to remove them.

There are several organic compounds, such as benzidine, 4,4'-diaminotolane and 2-aminoperimidine, which can be used as precipitants for sulfate. However, their use has been predominately for nephelometry and turbidimetry determinations which are discussed in the following paragraphs.

b. Titrimetry

There are many modifications of titrimetric methods of sulfate determinations. Most of the methods involve the pretreatment of the solution by passing it through a cation exchanger, or addition of suitable reagents to eliminate interferences from metal ions. Direct titrations with a barium salt, either barium chloride or barium nitrate, have been reported using various indicators, such as diphenylcarbazone (3), sodium alizarinsulfonate (4), and nitrochromeazo (5), etc. Potentiometric titrations using both barium and lead salts have been reported as well. Probably the most satisfactory titrimetric method is an indirect determination accomplished by adding a known amount of barium strontium, or lead salt and titrating the excess with a suitable reagent, such as ethylenediaminetetraacetic acid (EDTA) (6). There are other variations of indirect titrations too numerous to mention. However, in general, the titrimetric methods used to date do not lend themselves well to the determination of low concentrations of sulfates.

c. Colorimetry

Colorimetric methods for sulfate determinations follow the same general outline as found in gravimetry and titrimetry in that barium is added to precipitate barium sulfate. The methods usually involve one of three general procedures:

1) A known amount of barium salt is added to the sulfate solution and the excess barium is complexed with a reagent such as methylthymol blue (7). The remaining barium is then determined colorimetrically, thus allowing the amount of sulfate to be calculated:

$$\text{excess } Ba^{++} + SO_4^{+} \rightarrow BaSO_4\downarrow + \text{excess } Ba^{++}$$
$$\text{excess } Ba^{++} + MTB \rightarrow BaMTB$$

2) A known amount of barium is added to precipitate the sulfate followed by addition of a known amount of potassium chromate to precipitate the excess barium. The amount of sulfate present is determined by measuring the absorbance of the excess chromate:

$$Ba^{++} + SO_4^{=} \rightarrow BaSO_4\downarrow + \text{excess } Ba^{++}$$
$$\text{excess } Ba^{++} + K_2CrO_4 \rightarrow BaCrO_4 + \text{excess } CrO_4^{=} \quad \text{(yellow)}$$

3) A known amount of the insoluble barium chloranilate is allowed to exchange with the unknown sulfate solution to form barium sulfate and the highly colored acid chloranilate ion. The intensity of the color of the chloranilic acid is proportional to the amount of sulfate present.

$$BaC_6Cl_2O_4 + SO_4^{=} \rightarrow BaSO_4\downarrow + H_2C_6CL_2O_4 \quad \text{(violet)}$$

The exchange of an insoluble metal chloranilate with an anion to form chloranilic acid and precipitate the metal-anion salt is a very sensitive reaction.

d. Turbidmetry and Nephelometry

In these methods for sulfate determination, barium chloride, 4,4'-diaminotolane, 2-aminoperimidine, or benzidine, etc. are used to form a fine precipitate with sulfate. The basis of both measurements is the interaction of light with a fine suspension of particles. The differences in the methods are in the way this interaction is measured. In nephelometry, the radiation that is scattered by the particles is measured perpendicular to the axis of incident light. Turbidimetry, on the other hand, measures the amount of radiation that passes through the suspension and thus, the measurement is made along the axis of the incident light. Both of these methods are very sensitive to small amounts of sulfate, if the proper reagent is used.

All of the above methods assume that interfering sulfates have been eliminated by selective solubility techniques prior to analysis. All sulfates, no matter what the cationic form, will be detected by these methods, once they are solubilized.

Potential Instrumental Methods for Measuring H_2SO_4 Adducts

There are many commercially available instruments designed to monitor SO_2 and/or other volatile substances at low concentrations. The secret of applying most types of instruments to the measurement of H_2SO_4 aerosols is to develop an H_2SO_4 adduct that stabilizes the H_2SO_4 in the field, but can also be programmed to give off a stoichiometrically related substance for analysis. For instance, if the volatilized or decomposed adduct formed a sulfur containing species, then flame photometry could be used as the analysis method. If the adduct could be made to contain halogens, then the electron capture detector would be advantageous as the method of analysis. A totally organic structure could best be determined by the flame ionization detector.

The procedure for volatilization or decomposition of this type H_2SO_4 adduct consists of programming or isothermally setting the sample holder cell temperature sufficiently high to bring about the necessary change in state. The sample can then be channeled, through sufficiently heated lines, to the detector of the particular measuring instrument. Of course, the necessary precautions must be taken to prevent condensation, once the sample has reached the instrument.

Another possibility would be to find a solvent that selectively dissolves the H_2SO_4 adduct. If the fixed H_2SO_4 adduct is colored, or absorbs energy in the ultraviolet region, its intensity could be measured spectrophotometrically. Of course, this technique calls for an adduct that is sufficiently selective to react only with the H_2SO_4 portion of the sample. Any other sample interaction might cause erroneous readings, especially if the interference was at the same wavelength as the H_2SO_4 absorption adduct. Phosphoric acid aerosol could interfere with acid-base reactions, while the presence of additional sulfates could interfere with reagents designed to detect H_2SO_4. Selective solubility would also be beneficial as a preliminary step, to clean up the sample before injection into a chromatographic column. Selectivity would have to be one of the major criteria for choosing a solvent to function in this capacity.

Analytical techniques that presently appear feasible for the determination of H_2SO_4 adducts are presented in the following sections.

1. Flame Photometric Detector (FPD)

Several instrumental methods for sulfur measurement are available which make use of atomic emission and absorption characteristics. The one which is most convenient for measurement of a gas containing sulfur is the Flame Photometric Detector (FPD). Sample gas is fed onto an air-H_2 flame which causes sulfur atoms to emit their characteristic spectrum. A 374 nm optical filter selectively allows the sulfur light emission to reach a photomultiplier tube (older units are 395 nm filters, but these are subject to interference from hydrocarbons). This detector responds to any sulfur present, regardless of the oxidation state. The main advantage is the sensitivity, which ranges from the low nanogram range to about 1μ g of H_2SO_4.

Scaringelli and Rehme (8) developed a highly selective, sensitive method for determination of sulfuric acid aerosols in the atmosphere. The aerosol was collected by impaction or filtration, which separates the H_2SO_4 from the SO_2. The sulfuric acid was isothermally decomposed to sulfur trioxide under a nitrogen stream at 400°C. The liberated SO_3 was then converted to sulfur dioxide by reaction with hot copper. The SO_2 can be determined through spectrophotometric, coulometric, or flame photometric analysis. The only sulfate found to interfere is ammonium sulfate, which decomposes at approximately 300°C. The sensitivities of this method for colorimetric, coulometric, and flame photometric analysis are 0.3, 0.03, and 0.003 µg, respectively.

Willard (9) described an instrument based upon a technique similar to the one described above for the separation of H_2SO_4 from other volatiles using warm ultra-dry air instead of high temperatures. The lower temperature and the ultra-dry air enable the H_2SO_4 to be volatilized before $(NH_4)_2SO_4$, and thus eliminates it as an interference.

The FPD appears to offer an ideal compromise between selectivity and sensitivity.

2. Gas Chromatography

Chromatography is a physical method for the separation of the components of a mixture. The separation of the components is accomplished by a section of tubing packed with a stationary phase of large surface area. The stationary phase can be a solid or a liquid; hence, the names gas-liquid and gas-solid chromatography. Gas-solid chromatography is the technique of the stationary phase (solid) to separate the sample constituents by absorption. In gas-liquid chromatography, a thin film is spread over an inert solid, and the sample is partitioned in and out of this liquid film.

Qualitative analysis is accomplished by comparing the retention time (time from the injection of the compound of interest until it is registered by the detector) of the unknown compound with the retention time of standards. An identical retention time between sample and standard is an indication of the identity of the unknown species. However, qualitative analysis by chromatography is not an absolute measurement since it is possible for more than one compound to have the same retention time.

Quantitative analysis is accomplished by comparing the detector response of known concentrations with the detection response of the compound in the sample. This comparison is generally accomplished by peak area, peak height, or any number of methods referenced in the literature.

Butts and Rainey (10) made trimethylsilyl derivatives of various anions, including sulfates, and analyzed them by separation on OV-17 and SE-30 columns. Subsequent detection of the eluting derivatives was made by flame photometric and flame ionization detectors. The derivatives were prepared by placing 5 to 10 mg of the desired anion in a septum-capped vial and adding 200 μl each of dimethylformamide and bis(trimethylsilyl)-trifluoroacetamide. It appears feasible that H_2SO_4 adducts could be separated from analytically interfering species using adducts of sufficient volatility and columns of acceptable resolution.

Sulfur halides have been separated on Kel-F oil No. 3 (11) while organic sulfate derivatives have been analyzed on the ethyl ester of Kel-F 8114 acid, hexadecane (12,13), squalene (14), dinonylphthalate, and on tricresyl phosphate (15). These are just a few of the many types of columns used to analyze various sulfur compounds. The final column selection would ultimately depend upon the type of H_2SO_4 adduct formed and the specificity of the chromatographic detector utilized.

There are many types of sensitive chromatographic detectors that could be used to detect the eluting H_2SO_4 adduct. A list of sensitive chromatographic detectors (16) that could be utilized are presented in Table 5. Of course, the use of any detector could be restricted by the type of H_2SO_4 adduct being analyzed.

3. Mass Spectrometry

Mass spectrometry probably provides more molecular structure information than other analytical technique for the analysis of organic and inorganic species. The information generated from the mass spectrometer is usually sufficient to determine the structure of the species being examined empirically.

The mass spectrometer fragments a molecule to produce charged ions usually consisting of the parent ion and ionic fragments. The ion fragments are then sorted according to the mass-to-charge ratio. The mass spectrum is a measurement of all the different ion fragments and their relative intensities. No

TABLE 5. Gas Chromatographic Detectors (16)

Detector	Detectability (g/sec)	Comments	Applicability to H_2SO_4 Program
Thermal Conductivity	10^{-6}	Despite the relatively low detectability of this system, it is probably the most widely used for virtually any kind of substance.	Detects all volatile substances and is relatively insensitive. Very little use for this research.
Flame Ionization	10^{-12}	Nearly a universal detector; however, many gases of interest to environmentalists give little or no signal.	Very sensitive to all organic adducts. Sensitivity proportional to organic structure size. Good candidate for this research.
Alkali Flame Ionization	10^{-15}	Tremendous sensitivity for phosphorus compounds (pesticides). Otherwise, limited to compounds of nitrogen, sulfur, and halogens.	Fair potential for use in this research.
Flame Photometric	10^{-12}	Limited application to phosphorus and sulfur compounds.	Excellent potential for this research. Very sensitive to adducts containing sulfur. Specific for sulfur.
Electron Capture	10^{-14}	Very useful despite its limited sensitivity to halogenated compounds and other electronegative atoms	Fair candidate for this research. Extremely sensitive to halogenate adducts. Sensitivity proportional to electro negativity of adduct.
Helium Ionization	10^{-14}	A universal detector, but "limited" to low temperatures (<100°C) and to the type of column used. Very sensitive to leaks and contamination.	Very sensitive for all substances. Severe problems with column bleed. Fair potential for this research.
Mass Spectrometer	10^{-15}	Very expensive but essential to the absolute identification of components in many analyses. A universal detector.	Extremely sensitive to all compounds. Can distinquish individual species in a mixture. Good potential for use in this research.

two species exhibit the same spectrum, and thus mass spectra are suitable for positive identification of any species detected.

Qualitative interpretation of a "mass spectrum" consists of a critical examination of the fragment ions and piecing them together to form a molecule consistent with the original fragmentation pattern. Final identification is usually made by matching the unknown spectrum with the spectrum of a standard run on the same instrument. Quantitative interpretations are made by running a standard sample of known concentration and pressure, and calculating the response per unit of pressure based upon a particular ion fragment. The response of the sample can then be used to calculate the partial pressure of the sample constituent and, hence, its concentration.

The mass spectrometer offers a large potential for use as an H_2SO_4 adduct detection method. The detector offers both sensitivity and selectivity with the only requirement being that the sample exist in the gaseous state at the temperature and pressure existing in the ion source. The mass spectrometer is a highly sensitive device capable of seeing nanogram quantities of sample. Provisions are made on most mass spectrometer inlet systems for analysis of solid, liquid, and gas samples.

4. X-Ray Diffraction

Every crystalline substance scatters x-rays in its own unique diffraction pattern. The resulting diffraction pattern generated by a crystal is used to identify its specific structure. The intensity of each reflection and the angle at which it forms, supplies the basic information for the determination of the crystalline structure and its subsequent quantitation. It appears feasible, at this point, that x-ray diffraction could be used to quantitate sulfuric acid adducts, provided that they are crystalline in nature and present in sufficient quantity.

Robert, et al.(17) reported that graphite which has been treated with an oxidizing agent to remove electrons will allow sulfuric acid to insert between the carbon layers. The amount inserted was determined by x-ray diffraction. X-ray diffraction is not regarded as one of the more sensitive analytical techniques.

5. X-Ray Fluorescence

X-ray Fluorescence depends on the excitation of secondary x-rays characteristic of each element by adsorption of primary x-rays. The identification of these characteristic wavelengths and the measurement of their intensities constitute a method for qualitative and quantitative analysis.

Since x-ray fluorescence is responsive to an element, no matter in which state it is, it would be necessary to separate the H_2SO_4 adduct from other species containing the same element to be measured prior to analysis. Thus, while x-ray fluorescence is extremely sensitive, it would not be specific for an adduct, unless it could be insured that the element being measured in the adduct was not present in another form. Since, under normal conditions, x-ray fluorescence cannot be used on gases, a selective solvent would have to be found for the H_2SO_4 adduct, and the interfering species filtered off prior to analysis.

6. Atomic Absorption

In the atomic absorption method of analysis, solutions or dilute suspensions are atomized in a flame and reduced to elemental state. Atoms in the ground state of a given element absorb energy from a beam of light emitted by a hollow cathode lamp of the element sought. The instrument can be employed for flame emission spectroscopy, where spectral emission from ionized atoms of an element is measured.

Again, the same problem exists as with x-ray fluorescence, in that all states of a particular element are detected simultaneously. This would require a selective solvent approach to insure that interfering ions are eliminated prior to analysis. In addition, the H_2SO_4 adduct would have to contain a metal, so that the adduct could be detected by atomic absorption.

7. Infrared Spectroscopy

The infrared spectrum is one of the most characteristic properties of a compound. Characteristic spectra originate primarily from the vibrational stretching and bending modes within molecules when irradiated with electromagnetic energy in the infrared region. It is doubtful that infrared spectroscopy exhibits sufficient sensitivity to detect H_2SO_4 adducts in the range of interest to this research.

8. ESCA (Electron Spectroscopy for Chemical Analysis)

Electron spectroscopy is performed on the inner shell electrons emitted from samples irradiated with x-rays. The kinetic energy of the ejected electrons is equal to the energy of the incident photons hν less the electron binding energy E_b. A measurement of the electron kinetic energy is thus a means of identifying the elements in the sample and the quantity of electrons is proportional to the concentration.

Stein (18) reported that ESCA is the most sensitive analytical technique at the present time, able to detect 10^{13} sulfate/sulfur atoms per cm^2. Unfortunately, this is a new procedure, the equipment is expensive, and the technique uncommon. However, ESCA merits consideration as a possible analytical method for the H_2SO_4 program.

9. Chemiluminescence Monitors

Dzubay, Rook and Stevens (19) have described a technique using a chemiluminescence monitor to measure H_2SO_4 aerosol concentration. The technique consists of reacting the H_2SO_4 with excess ammonia and converting the unreacted ammonia to NO gas in a gold or copper oxide converter. Sensitivity of this method for H_2SO_4 aerosol is said to be approximately 20 $\mu g/m^3$. Background levels of NO and NO_2 have been shown to have an effect.

Commercial chemiluminescence instruments could probably be utilized with minimal alterations, to monitor H_2SO_4 aerosol, if an H_2SO_4 adduct could be developed that would decompose or valatilize to give off NO or NO_2.

10. Spark Replica Technique

Stickney and Quon (20) have developed a spark replica technique for measurement of sulfuric acid nuclei. This technique involves exposure of a polycarbonate film to an acid aerosol and counting the number of defects or holes developed in the film with a spark replica counter. Sparking is induced through the use of the film as the dielectric material of a capacitor, and impressing a voltage across this capacitor. The concentration of nuclei is an exponential function of the number of counts (holes) recorded. The minimum detectable concentration is 10^4 nuclei/cm^3. The specificity has not yet been determined.

Analytical Methods Conclusions

Each of the analytical techniques discussed has inherent advantages and disadvantages for analyzing sulfuric acid adducts. Some of the techniques discussed are fairly selective but do not exhibit the necessary sensitivity, while for others, the converse is true. The final choice in selecting an analysis method will depend upon the type of H_2SO_4 adduct to be analyzed. Criteria such as the specificity of the adduct formation and the chemical and physical characteristics of the H_2SO_4 adduct will have to be evaluated with each potential analysis method in order to determine which combination is best. The optimum choice will be a trade off between selective analyzability and adduct sensitivity. The extent of this trade off will depend on the nature of the particular sulfuric acid adduct under examination. Theoretically, it appears that the sensitive, sulfur specific flame photometric detector has the best specifity to sensitivity ratio for sulfuric acid adduct measurement.

REFERENCES - APPENDIX B

1. Gehard, E. and F. Johnstone, "Microdetermination of Sulfuric Acid Aerosol," *Anal. Chem.*, *27*, 702 (1955).

2. Lodge, J., J. Ferfueson and B. Havlik, "Analysis of Micron-Sized Particles: Determination of Sulfuric Acid Aerosol," *Anal. Chem.*, 32, 1206 (1960).

3. Lewis, W. M., "Determination of Sulfate and Chloride in Water by Direct Titration, Using Diphenylcarbazone as Indicator," *Proc. Soc. Water Treat. Exam.*, 16, 287 (1967).

4. Ceausescue, D. and M. Asteleanu, *Hidroteh Geospodaririea Apelor Meteorol (Bucharest)*, *11*, 278 (1966); CA, 66, 5658K (1967).

5. Basargin, N. N. and A. A. Nogina, "The Determiantion of Sulfates in Natural and Boiler Feed Water in the Presence of Phosphates by the Direct Titration with Barium Salts by using Nitrochromeazo as Indicator," *Zh. Anal. Khim.*, *22*, 394 (1967).

6. Effenberger, M., *Fortschr. Wasserchem. Ihrer Grenzgeb.*, *1*, 173 (1964); CA *67*, 36312 a (1967).

7. Lazrus, A., E. Lorgane and J. P. Lodge, Jr., "Automated Microanalyses for Total Inorganic Fixed Nitrogen and for Sulfate Ions in Water," *Advan. Chem.*, *73*, 164 (1968).

8. Scaringelli, F. P. and K. A. Rehme, "Determination of Atmospheric Concentrations of Sulfuric Acid Aerosol by Spectrometry, Coulometry and Flame Photometry," Anal. Chem., 41, 707 (1969).

9. Willard, Richard L., Preprint, National Meeting Division Water, Air and Water Chemistry, Am. Chem. Soc. (1973).

10. Butts, W. C. and W. T. Rainey, "Gas Chromatography and Mass Sepctrometry of the Trimethylsilyl Derivatives of Inorganic Ions," Anal. Chem., 43 (4), April (1971).

11. Campbell, R. H. and B. J. Gudzinowicz, "Separation of Some Fluorocarbon and Sulfur-Fluoride Compounds by Gas-Liquid Chromatography," Anal. Chem., 33, 842 (1961).

12. Dresdner, R. D., T. M. Reed, T. E. Taylor and J. A. Young, "Six and Twelve Carbon Fluorocarbon Derivatives of Sulfur Hexafluorides," J. Org. Chem., 25, 1464 (1960).

13. Dresdner, R. D. and J. A. Young, "Some New Sulfur-bearing Fluorocarbon Derivatives," J. Am. Chem. Soc., 81, 574-577 (1959).

14. Davis, A., A Roadi, J. Michalovic and H. Josphe, "Applications of Gas Chromatography to Phosphorus-Containing Compounds," J. Gas Chromatog., 1, 23 (1963).

15. Panek, K. and K. Murda, "Continuous Measurement of the Radioactivity in the Separation of Compounds Labeled with ^{36}S by Gas-Liquid Chromatography," Radiokyhimiya, 7, 246 (1965).

16. Gosink, T. A., "Gas Chromatography in Environmental Analysis," Envrion. Sci. and Tech., 9 (7), July (1975).

17. Robert, N. C., M. Oberlin and J. Mering, "Lamellar Reactions in Graphitizable Carbons," Chem. Phys. Carbon, 10, 141 (1973).

18. Stein, H. P. and C. D. Hollowell, "Measurement of Atmospheric Sulfate," NTIS, LBL-2162, U.S. Department of Commerce, Springfield, VA.

19. Dzubay, T. G., H. L. Rook and R. K. Stevens, Analytical Methods Applied to Air Pollution Measurements, ed. by Robert K. Stevens and William F. Herget, Ann Arbor Science, Ann Arbor, Michigan, 71 (1974).

20. Stickney, J. and J. Quon, "Spark Replica Technique for Measurement of Sulfuric Acid Nuclei," Environmental Sci. and Tech., 5, 1211 (1971).